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DEPARTMENT OF COMMERCE

TECHNOLOGIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 165

ENAMELS FOR SHEET IRON AND STEEL

BY

J. B. SHAW, Assistant Ceramic Chemist

Bureau of Standards

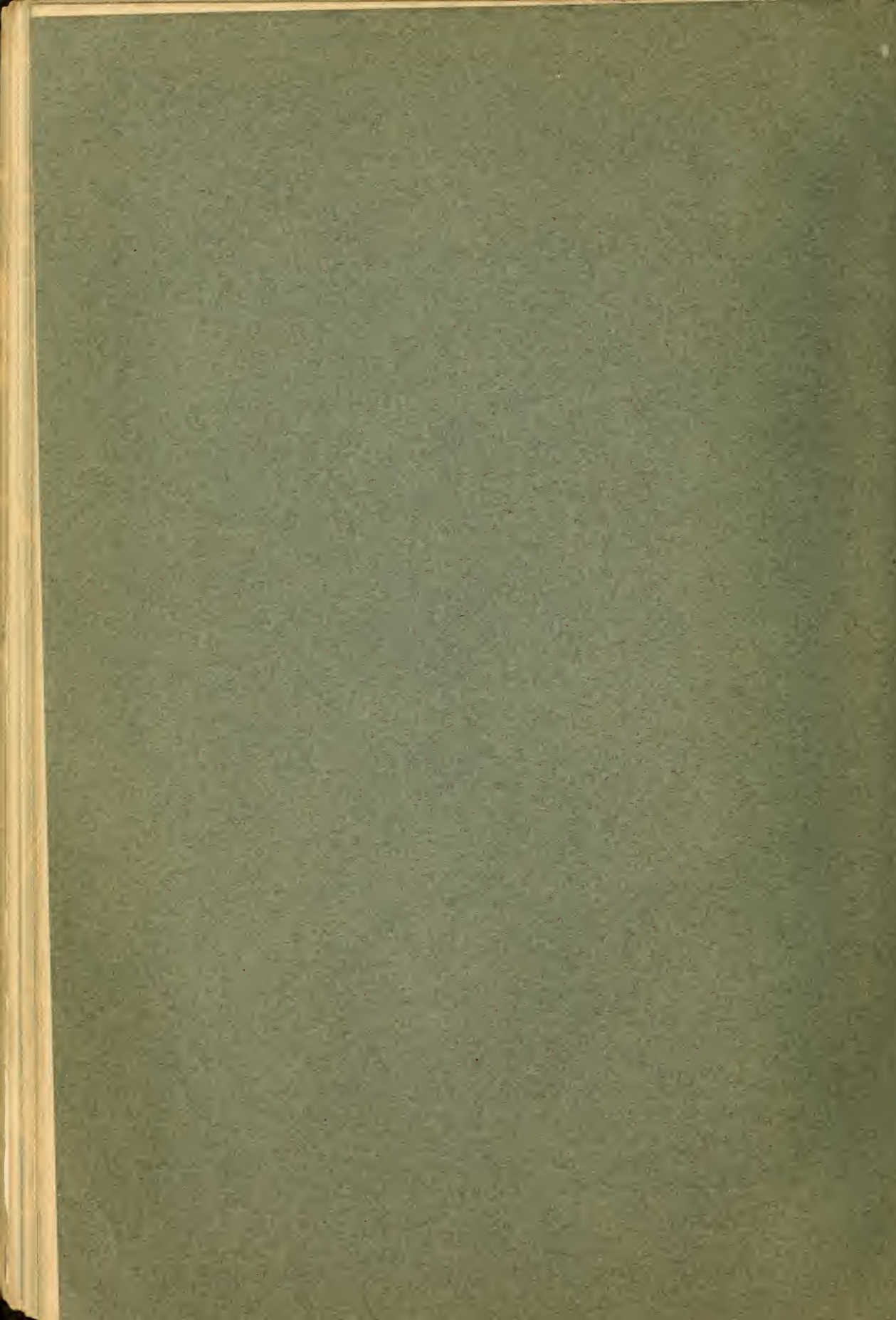
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ERRATA

Page 7, last table, column three, line one: The values given are as in the original. Evidently they should be 0.40 to 0.60.

Page 25, line four of tabulation: The values given are as in the original. Evidently there is some error.

Page 28: The first equation should read



Page 61, Table 4: The formula weight of boric acid should be 124. The formula weight and melted weight of cobalt oxide should be 241.

Page 62, Table 4: The melted weight of cryolite should be 286.

Page 64: The table should be as follows:

322.39

6.80 70

60.36 50

28.70 57

7.29 51

19.70 77

7.80 8

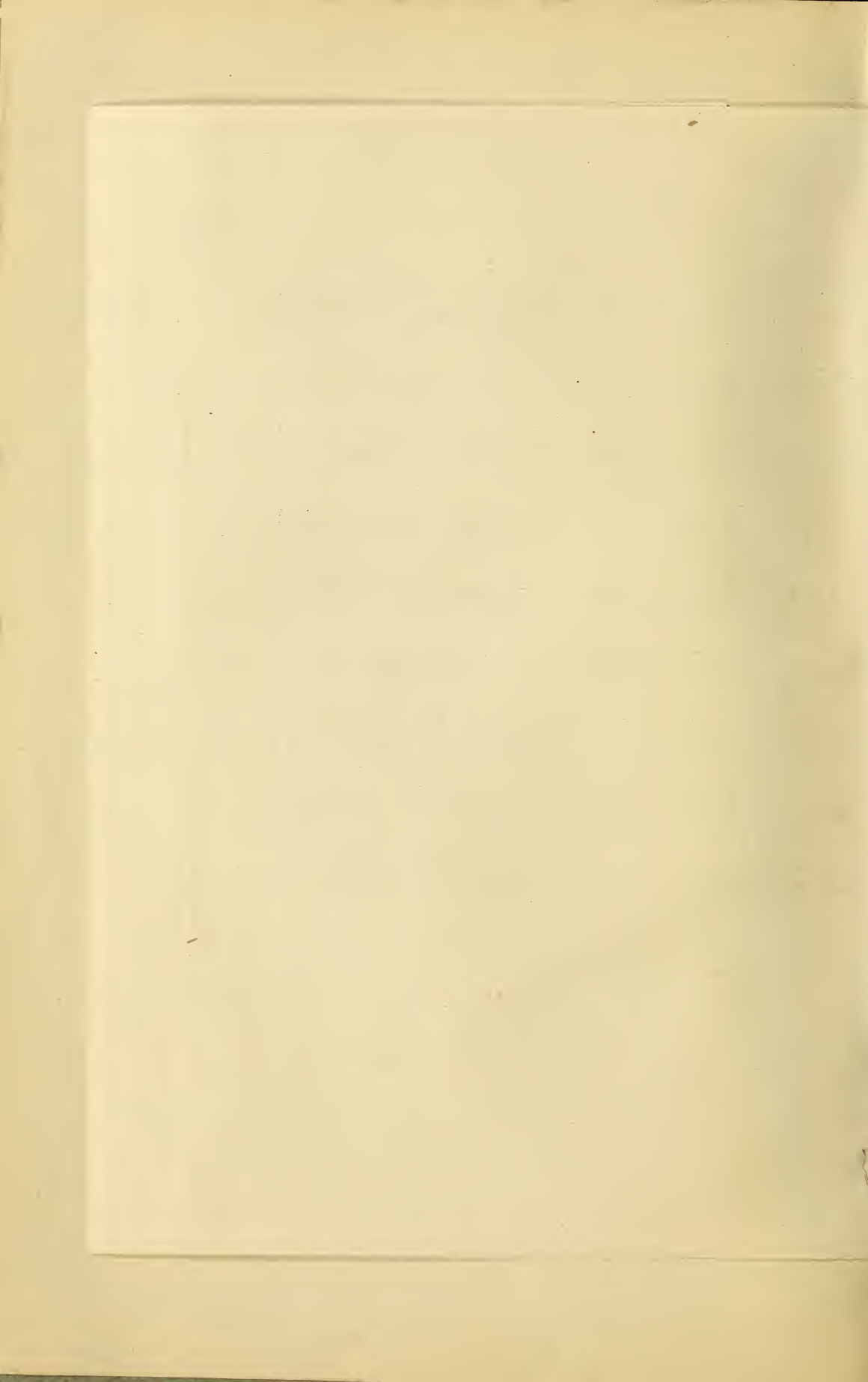
+6.20 10

95.50 52

50.04 6

Baton weight

Formula										Material used	Molec- ular parts	Form- ula weight	Batch weight
K ₂ O	Na ₂ O	CaO	BaO	ZnO	Al ₂ O ₃	SiO ₂	B ₂ O ₃	F	Sb ₂ O ₃				
0.09	0.62	0.10	0.10	0.09	0.20	1.60	0.50	1.52	0.10				
.0909	.54	{Feldspar, K ₂ O,} {Al ₂ O ₃ , 6SiO ₂}	0.09	X556	50.04
....	.2511	1.06	{Borax, Na ₂ O,} {2B ₂ O ₃ , 10H ₂ O....}	.25	X382	95.50
....	.37	0	{Cryolite, 6NaF,} {Al ₂ F ₆}	.11	X420	46.20
....	.3311	1.32				
....	.04	020	{Fluorspar CaF ₂10	X 78	7.80
....1020				
....	0	0	{Barium carbonate,} {BaCO ₃}	.10	X197	19.70
....10				
....	0	{Zinc oxide, ZnO..	.09	X 81	7.29
....09				
....	0				
....10	{Antimony oxide, } {Sb ₂ O ₃}	.10	X287	28.70
....	1.06	0	{Flint, SiO ₂	1.06	X 60	60.36
....	0				
....	.04	{Sodium nitrate, } {(NaNO ₃) ₂}	.04	X170	6.80
0				322.39



A CLASSIFICATION OF SHEET STEEL ENAMELS¹

R. R. Danielson²

TECHNOLOGIC PAPERS OF THE
BUREAU OF STANDARDS, No. 165

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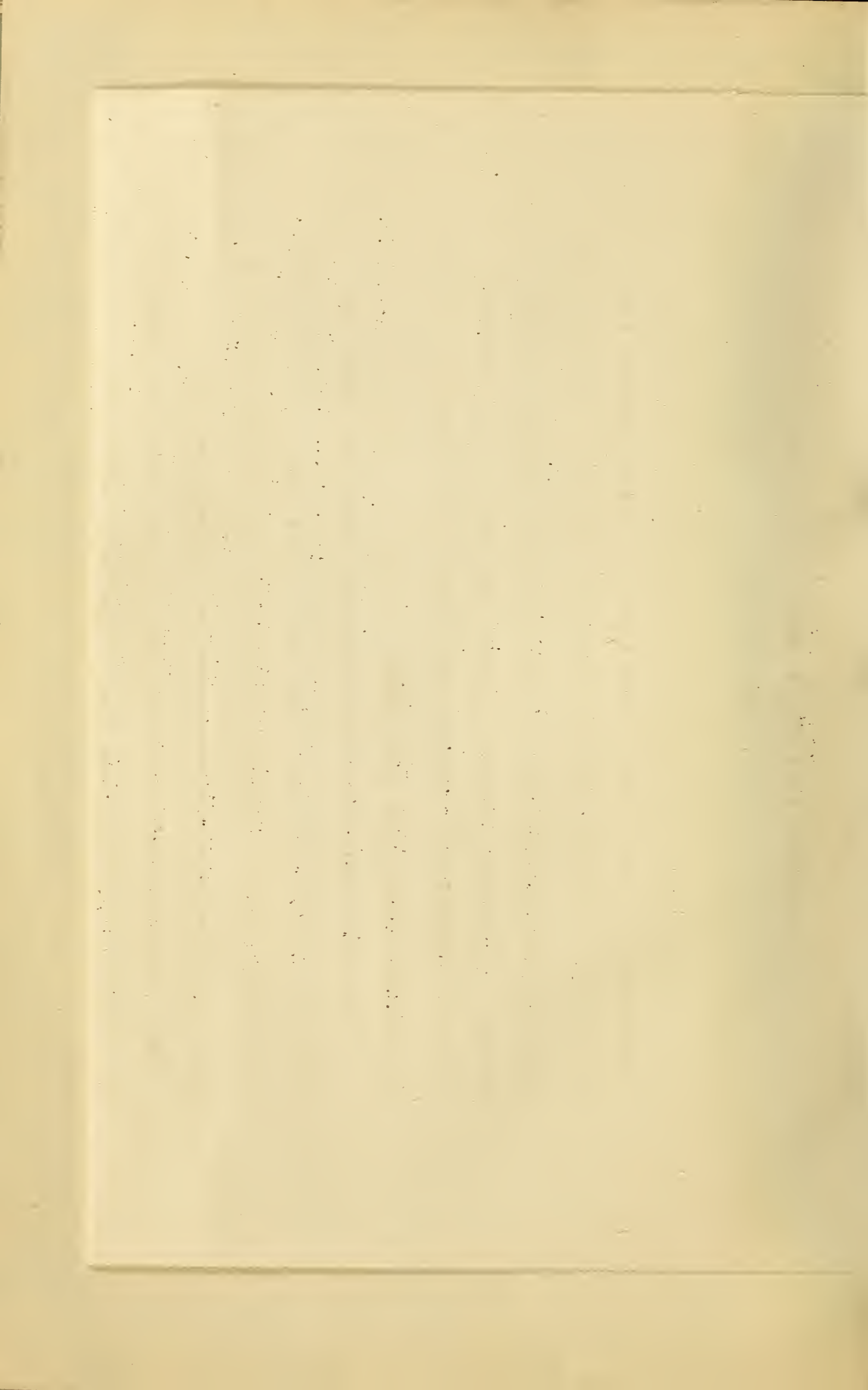


Table 1. - Gray Ware Enamels

Batch Compositions of Frits

A	B	C
---	---	---

[illegible]

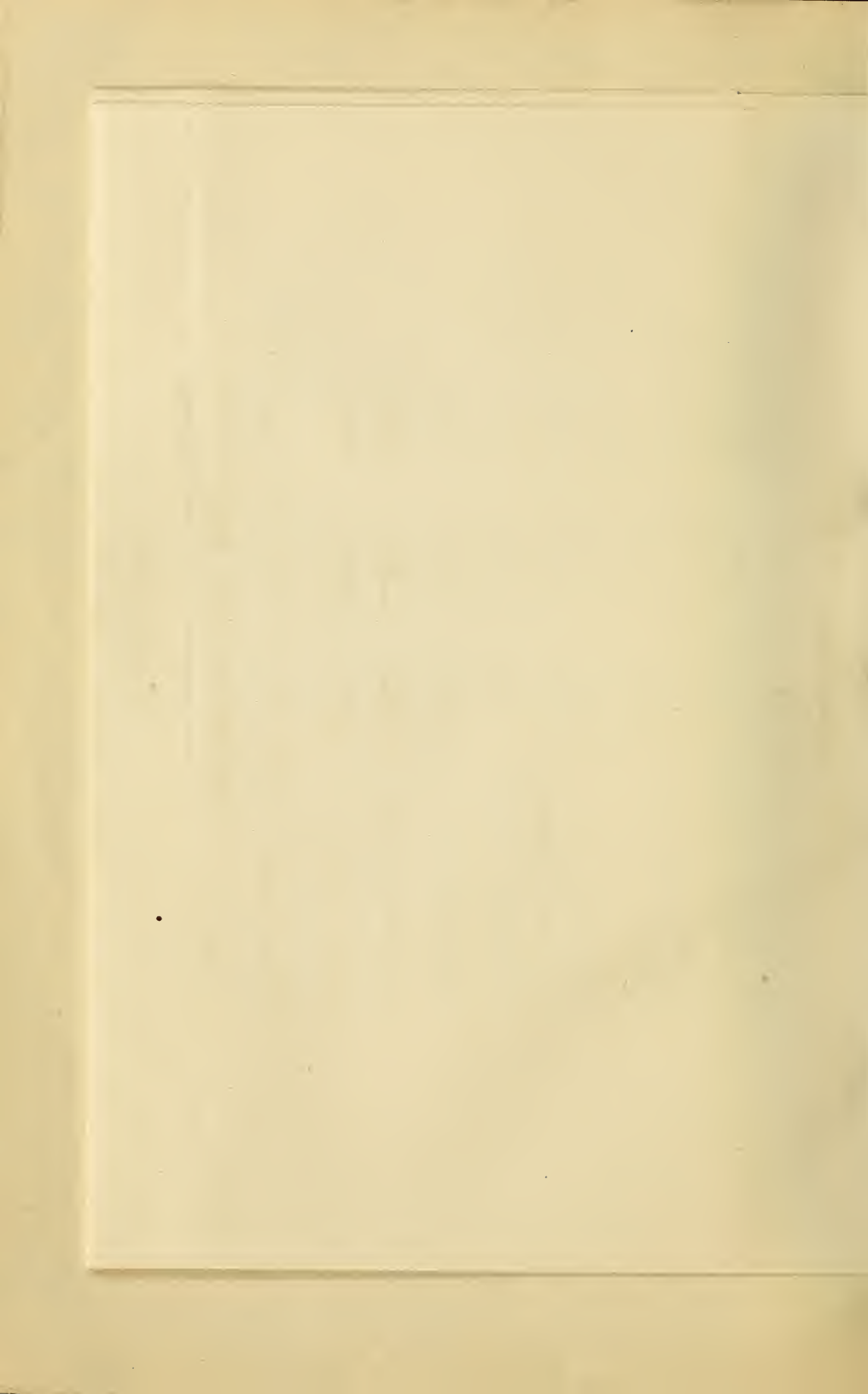


Table 3 White Cover Enamels
Batch Compositions of Frits

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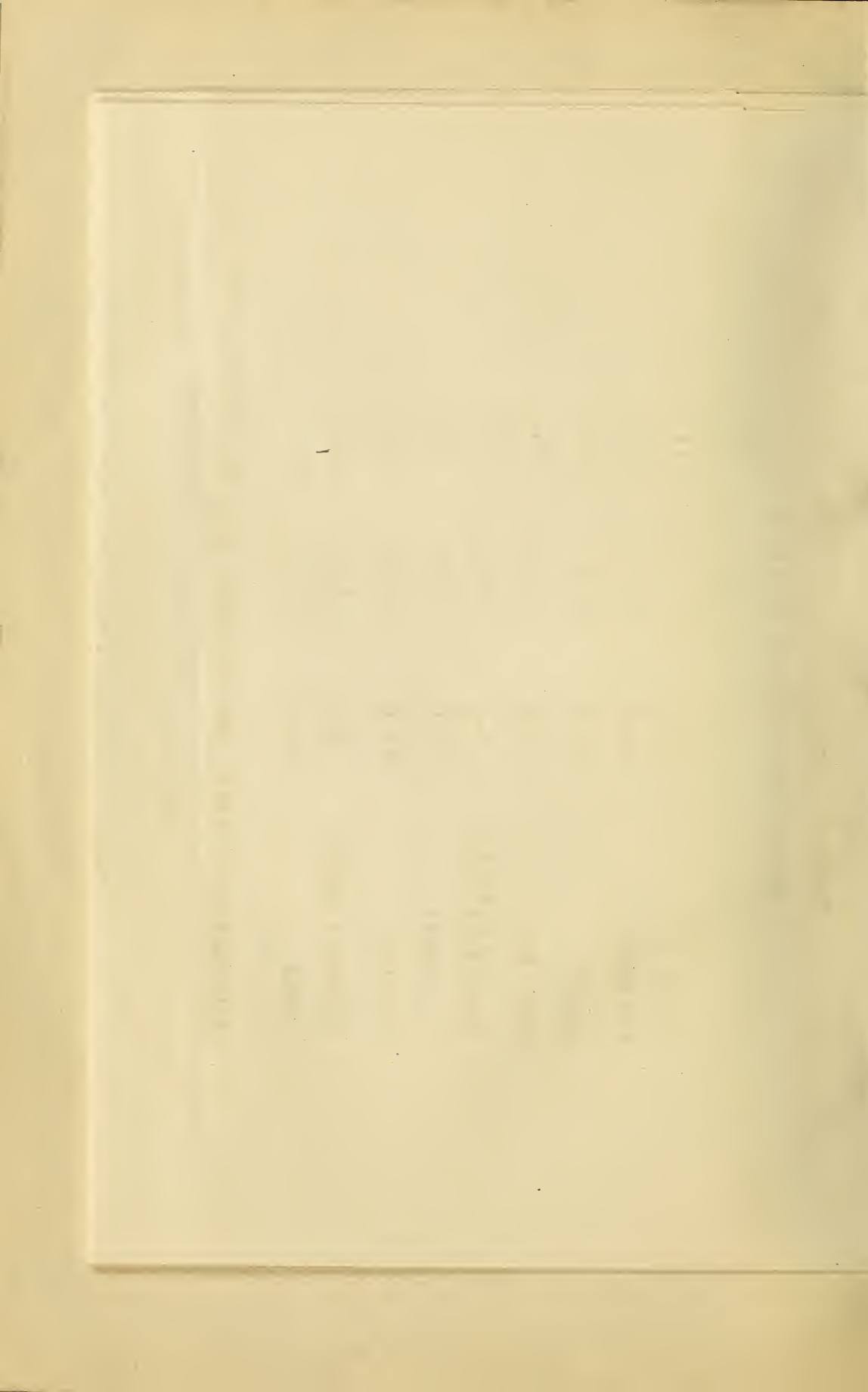
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Page 61, Table 4: The formula weight of boric acid should be 124. The formula weight and melted weight of cobalt oxide should be 241.

Page 62, Table 4: The melted weight of cryolite should be 286.

Page 64: The table should be as follows:



White enamels A, B, and C, given in Table 3, show a transition from those of the old German type to those now in use in American practice. There is a decrease in fluorspar

Formula										Material used	Molec- ular parts	Form- ula weight	Batch weight
K ₂ O	Na ₂ O	CaO	BaO	ZnO	Al ₂ O ₃	SiO ₂	B ₂ O ₃	F	Sb ₂ O ₃				
0.09	0.62	0.10	0.10	0.09	0.20	1.60	0.50	1.52	0.10				
.0909	.54	{Feldspar, K ₂ O,} {Al ₂ O ₃ , 6SiO ₂}	0.09	X556	50.04
.....	.2511	1.06	{Borax, Na ₂ O,} {2B ₂ O ₃ , 10H ₂ O.....}	.25	X382	95.50
.....	.37	0	{Cryolite, 6NaF,} {Al ₂ F ₆}	.11	X420	46.20
.....	.3311	1.32				
.....	.04	020				
.....1020	{Fluorspar CaF ₂ ...}	.10	X 78	7.80
.....	0	0				
.....10	{Barium carbonate,} {BaCO ₃}	.10	X197	19.70
.....	0				
.....09	{Zinc oxide, ZnO..}	.09	X 81	7.29
.....	0				
.....10	{Antimony oxide, } {Sb ₂ O ₃}	.10	X287	28.70
.....	1.06	0				
.....	{Flint, SiO ₂}	1.06	X 60	60.36
.....	.04	0				
.....	{Sodium nitrate, } {(NaNO ₃) ₂}	.04	X170	6.80
0				322.39

ENAMELS FOR SHEET IRON AND STEEL

By J. B. Shaw

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I. INTRODUCTION

Within the last 20 years the ceramic industries of the United States have made great improvements in the quality of their products, due to the abandonment of the rule-of-thumb methods which marked the beginning of the industries and to the application of scientific principles in the manufacturing processes. Many volumes have been written describing the results of extensive investigations of cause and effect; as a result of these extended researches both in factory and laboratory the sum total of known facts regarding the silicate industries has been greatly augmented. Therefore, the physical and chemical properties of ceramic products can be modified and largely controlled at will. By correlation of data obtained by many different investigators manufacturers of ceramic wares are not only eliminating waste in their factories, but are also developing their products to a high state of perfection. It should be said, however, that, while much has been learned, very much more is to be learned even in the most advanced of the industries.

From the standpoint of mechanical equipment the sheet iron and steel enameling industry has been probably the most progressive of all ceramic industries in the United States. The presses and machinery used for working the steel and forming the shapes

are unsurpassed in ingenuity by those used in any other industry, and are constantly being improved. In this respect the sheet-metal enameling industry of this country has led the world.

In the strictly ceramic lines of the industry having to do with the preparation and application of the enamels progress has been less rapid. Up to a few years ago there was very little cooperation. There was very little research work carried on, and this little was seldom reported in print. Very recently there has been a decided change in this respect. Representatives of the enameling industry have been joining the ceramic technical societies; have been contributing rather liberally to the journals of these organizations; and have been showing a decided interest in developing the technology of sheet-metal enameling. The leading manufacturers of the country are realizing that the sheet-iron enameling industry has reached the limit of development possible, so long as it depends upon formulas rather than upon men with the technical training which will enable them to improve and manipulate these formulas to meet varying conditions. The sum total of known facts about enamels and their application is very small. There is room for enormous expansion and improvement in the industry, and this can be accomplished only by active cooperation and research. In collecting data for this paper an effort has been made to obtain reliable and authentic information wherever available and to correlate it in such a manner as to shed some light on the problems encountered by enamellers.

II. PROPERTIES AND PREPARATION OF STEEL FOR ENAMELING

1. PHYSICAL AND CHEMICAL REQUIREMENTS

In commenting upon the kind of steel used in European practice, Julius Grünwald says:¹

For acquiring a well-finished article the use of first-class, box-heated, doubly forged basic Martin steel is indispensable. Inferior kinds of steel, such as are often used for some cheap folded articles, are in reality of no advantage when one considers the greater percentage of imperfect goods produced and the insignificant difference in price between the doubly forged and the singly forged varieties of sheet steel. Consequently the manufacturers use almost throughout only the very best German brands, which are entirely equal to the English forged preferred earlier. The following is regarded as a favorable composition for a good forged steel:

	Per cent
Carbon.....	0.05 to 0.08
Phosphorus less than.....	.03
Manganese.....	.25 to .35
Silicon, small amounts.....	.02

¹ Grünwald, J., *Technology of Iron Enameling and Tinning*, Griffin; 1912.

The strength test must show the following results:

Coefficient of tenacity.....	35 to 38 kg/mm ²
Coefficient of elasticity.....	30 to 35 per cent
Coefficient of contraction.....	60 per cent
Specific gravity.....	7.6 to 7.8

It is generally accepted as a fact that in no other country has the manufacture of steel reached a higher state of refinement than in the United States. Some of the largest manufacturers in the country supplying the enameling trade have the following to say with regard to steel for enameling purposes:

No special grade of steel is manufactured to be used exclusively for enameling purposes, but steel manufacturers do make a steel, used quite extensively by the manufacturers of enameled ware, which is particularly adapted for deep-stamping purposes, and in which the different impurities are kept low to avoid excessive breaking. The annealing of such steel also has an important bearing on the quality.

It has been found that standard soft steel for deep-stamping purposes, made by either the Bessemer or open-hearth process (depending largely on the severity of the drawing operation which it is required to meet) and having about the following composition, seems to give the best results when properly treated while undergoing processes:

	Per cent
Carbon.....	0.08 to 0.12
Phosphorus.....	.040 and under
Manganese.....	.30 to 0.50
Sulphur.....	.05 and under
Silicon.....	.025 and under

There is nothing peculiar in the rolling of the material into sheets, the regular practice of alternate heating and rolling being followed until the required gage is obtained. The gages used are generally within the range of No. 20 to 28 United States standard gage.

After rolling, the packs, which contain a number of sheets, are sheared, and the sheets are opened or separated; then they are subjected to a pickling operation, embodying an exposure of approximately five minutes in a bath of sulphuric acid containing approximately 5 per cent free acid, at a temperature of approximately 180° F. This is for the purpose of entirely removing all mill scale formed during the rolling process.

When the pickling operation has been completed, the sheets are transferred to a water bath and by agitation therein freed from adhering acid to the greatest possible extent. The sheets are then subjected to an annealing operation, under cover, at a temperature of approximately 1400° F for a period of from 14 to 16 hours.

When annealed and cooled the sheets are inspected, and those rejected which are determined to be unsuitable for the stamping and enameling operation. These rejections are confined entirely to mechanical defects, such as thick edges, which interfere with satisfactory drawing, and surface defects and imperfections which might interfere with this or with the enameling operation.

Practically pure iron is a recent development in the steel industry. The operations required in making it are the same as those in making any other grade of open-hearth steel, but due to the fact that the product is higher in iron (Fe) and lower in other ingredients which go to make up the body of other steel, the process requires higher temperatures for melting and more inten-

sive open-hearth treatment to eliminate the phosphorus, manganese, sulphur, and silicon.

This iron has a smooth surface and is uniformly free from blisters and irregularities in texture. Its high iron content and low phosphorus and silicon contents make it very ductile, and therefore well adapted to deep drawing. In view of the fact that much of the loss in the enamel industry results from breakage in drawing, this factor is one of importance. As regards the ability of this iron to take a coating of enamel better than other steel, no exact data are available from which to judge. Theoretically, one disadvantage which it has is the smoothness of the surface. However, it has been used successfully in a number of enameling plants.

A manufacturer of heavy-gage, enameled-steel containers made comparative tests on steels of the following compositions:

No.	Carbon	Sulphur	Phosphorus	Manganese
33568.....	0.12	0.018	0.008	0.35
33457.....	.10	.025	.010	.42
34421.....	.15	.022	.009	.33
33613.....	.13	.025	.011	.46
33590.....	.10	.023	.009	.35

The five steels were selected for test with a view to finding one which could combine qualities meeting several requirements, namely, flanging, welding, forming into different shapes, and enameling.

It was found that about 10 per cent of the sample sheets which were very good for enameling broke down under the other tests. No. 34421 was selected as most satisfactory and was adopted for use. Several thousand tons of it have since been enameled with excellent results. Steel having the other four compositions has many defects.

R. D. Landrum ² gives the following as the best composition of steel for enameling purposes:

	Per cent
S.....	0.040 to 0.050
P.....	.030 to .090
Si.....	.01
Mn.....	.060 to .040
C.....	.10

The following compositions are recommended or sold for use:

Carbon	Phosphorus	Manganese	Sulphur	Silicon	Authority
0.10.....	0.030 to 0.090...	0.040 to 0.060..	0.040 to 0.050...	0.01.....	Landrum
.15.....	.009.....	.33.....	.022.....	A manufacturer of heavy containers American practice Grünwald
.08 to 0.12...	.040 and under	.30 to .50...	.05 and under.	.025 and under.	
.05 to .08...	Less than .03...	.25 to .35...02.....	

² Landrum, R. D., Methods of Analysis for Enamel and Enamel Raw Materials, Trans. Am. Ceram. Soc., 12, p. 173.

The table includes a comparatively wide range of compositions, showing a wide diversity of opinion as regards the proper composition of steel for enameling purposes.

One is led to the conclusion that the chemical composition of the steel has no important bearing on its ability to take and hold a coating of enamel successfully. This seems quite reasonable in view of the fact that cast iron, containing large quantities of silicon, phosphorus, manganese, and carbon, is easily enameled, and steels of great variety in composition, running from those highest in matter other than iron to the purest wrought iron, are successfully enameled for various purposes.

Experience in enameling many different kinds of ware confirms the above conclusion. There is only one type of defect in enameled ware that can properly be attributed to bad steel, and that is the blistering which comes from a pocket of gas or slag being rolled into the sheet. These blisters result from poor steel and very frequently reveal themselves during the pickling operation. It frequently happens that the enameler, in trying to clear himself of the blame for defective ware, attributes the trouble to defective steel. To make a cry of poor steel is an easy way to shift the responsibility for poor ware; but if a piece of steel is free from blisters and is properly cleaned, it is only a remote possibility that any defects in the enamel coating can be properly attributed to it, regardless of its chemical or physical properties.

When it comes to consideration of the action of steel in drawing and stamping, the chemical and physical properties are highly important. In order to stand deep drawing, steel must possess a high degree of ductility and high tensile strength. These properties are imparted to the steel by giving it the proper chemical composition and the proper treatment during the process of manufacture.

2. SAND BLASTING

The preparation of the steel for enameling consists in giving it such treatment as is necessary to leave a clean surface, free from any foreign matter that will injure the enamel when applied and burned. The treatment required depends upon the nature and size of the piece of ware and the kind of foreign matter that is to be removed.

The sand blast is used in cleaning large ware and such as can not be easily cleaned by pickling. When the sand blast is used, no other treatment is required, since grease, rust, and any other

foreign matter is readily removed by it. This is the most effective method of cleaning steel and one that gives an excellent surface for enameling. For small pieces it is much more expensive than pickling, and it is economical only in making large pieces or special shapes of comparatively high value.

3. TREATMENT PRELIMINARY TO PICKLING

Nearly all light steel ware is cleaned by the pickling process. The preliminary treatment before the ware is placed in the pickling acid varies. Grease and carbonaceous matter must be removed from the ware before placing in the pickling solution, and three general methods are in use for doing this; scaling, washing in caustic alkali solutions, or the use of proprietary cleaning compounds.

(a) *SCALING*.—Scaling or heating the ware to redness is the method most generally employed. During the process of shaping the ware from the sheet of steel it invariably collects grease from machinery and workmen's hands, and one method of removing such carbonaceous matter is to burn it off. Especially is this the case when handling large numbers of small pieces. To do this, the ware should be carefully stacked on grates in such a manner as to admit free access of air to all parts of every piece of ware. Care must be taken to prevent flat surfaces from coming into contact with each other, and space must be provided between the different pieces of ware to admit sufficient air to completely oxidize all carbonaceous matter present. It must be remembered that the heat treatment forms an iron scale which must subsequently be removed by acid, and consequently the time and temperature should not be carried beyond that necessary to burn off the oil.

The primary object in scaling is to burn off the carbonaceous matter, but this heat treatment does undoubtedly have the effect of changing the structure of the steel and relieving strains set up during the forming. Grünwald³ attaches considerable importance to the benefit derived during this heat treatment through liberation of the strains set up during the forming of the ware. While there is ample proof that these strains do exist and are vital factors affecting the property of the steel for drawing, there is no evidence to show that they affect the ware as regards the appearance of enamel or its adherence to the metal. As evidence that these strains do affect the enamel, it is generally pointed out that the

³ Grünwald, J., *Technology of Iron Enameling and Tinning*.

angles and sharp corners are the most difficult places on which to make enamel stick; but precisely the same thing is true of cast-iron enamels, in which case no strains exist in the corners any more than those which may exist on the flat surfaces.

As a result of an extensive series of experiments on pickling operations, Grünwald concluded that the proper temperature for heating the ware in scaling is between 650 and 750° C. If the temperature is much below 650° C, the oil will not be completely burned off. If the temperature exceeds 750° C, the amount of scale formed on the surface is excessive, increasing unnecessarily the cost of pickling. He shows that the time required for pickling increases with the duration and temperature of heating the ware; thus only 3 minutes are required for pickling with hydrochloric acid, 10° Baumé, a sheet-iron disk that has been heated at 760° C, while 14 minutes are required for pickling a sheet heated for the same length of time at 940° C. When sulphuric acid, 110° Baumé at 60° C is used, the time required for pickling is increased.

(b) REMOVING GREASE WITH CAUSTIC SODA.—Caustic soda or potash may be used for removing fatty materials, especially if they are present in small amounts. In this process the steel article is immersed in a boiling solution of caustic soda or potash and allowed to remain for a few minutes. It is then taken out and washed free from alkali in clear water. This precaution is necessary because the adhering alkali solution would rapidly neutralize the pickling acid into which the steel is next placed for the removal of rust and other deleterious impurities.

(c) USE OF PROPRIETARY CLEANING COMPOUNDS.—There are on the market a number of prepared chemical cleaners which may be substituted for caustic soda and which give excellent results in the removal of grease from ware to be enameled. These cleaners may be composed of one or several of the following materials: Sodium hydroxide, sodium carbonate, ammonium carbonate, borax, trisodium phosphate, sodium silicate, soaps, and rosin, which, in the presence of caustic alkalies, forms soaps.

This method of removing grease with chemicals should not be employed in cleaning ware which becomes coated with heavy mineral oils during the manufacturing process, because it is difficult to remove these oils. On large flat pieces and such as are not handled much during the shaping, the amount of oily matter to be removed is small, and this process can be used to advantage in such cases.

4. PICKLING

After the oil and carbonaceous matter have been removed from the surface, it is necessary to remove all rust and oxide of iron. As has been noted, in the scaling and annealing of the steel there is always more or less oxide of iron formed on the surface, and this must be removed before the ware can be successfully enameled. The pickling solution used is one of either sulphuric or hydrochloric acid.

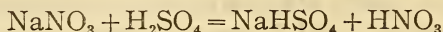
(a) PICKLING VATS.—One of the most troublesome problems in the enameling plant is to get satisfactory vats for holding the pickling solution. General practice is to use double tanks made of soft pine with a space of about 2 inches between the inner and outer walls. This space is filled with pitch, which is melted and poured into place. This is probably the most satisfactory form of tank for use where the acid is not heated, but if a hot acid bath is used the pitch will soften and allow the acid to work its way through to the outside. Wooden tanks lined with sheet lead have been tried, but they are expensive and the rough treatment to which they are subjected in placing ware in them and taking it out soon destroys them.

A satisfactory tank for enameling work is made from good quality cypress, at least $2\frac{1}{2}$ inches thick and braced throughout with wood. If iron bracing is used, it should be renewed at frequent intervals. The threads on iron rods are very rapidly destroyed by acid vapors, and when the bracing gives way the tank very soon begins to leak. It is almost impossible to stop such a leak. If a tank is made of cypress and is kept well braced it will last almost indefinitely.

(b) PICKLING ACID.—The question of what is the best acid to use for pickling steel is a mooted one. Both sulphuric and hydrochloric (muriatic) acids are used, and there seems to be little choice between them when everything is considered. Sulphuric is undoubtedly the cheaper, but it must be heated to get it to work as rapidly as does the hydrochloric when cold, and the fumes arising from hot sulphuric acid cause great inconvenience to the workmen. Proper precautions may be taken to carry off the fumes, and this not only has the advantage of saving the workmen from discomfort, but also keeps the acid fumes out of the other parts of the factory, and thus prevents corrosion of metal parts. Even when cold hydrochloric acid is used it is of great importance that the pickling room be isolated from the

other departments, and it is also advisable to use fans to draw off the acid vapors.

Niter cake has come into extensive use for pickling in recent years. It is a by-product obtained in making nitric acid from sodium nitrate and sulphuric acid, according to the following reaction:



The acid-sodium sulphate or niter cake is shipped in bulk, thereby avoiding the use of carboys. Sulphuric acid is the active agent in using this material, it being liberated when the salt is dissolved in water. It is necessary to heat the pickling solution in this case, as in the use of sulphuric acid.

Acid vapors from the pickling room are injurious both to ware which has not been coated with enamel and to ware which has a coat of enamel on it, but requires a subsequent coating. If ware which has not been enameled is subjected to the acid vapors it is likely to rust, and this will cause defective ware. If ware coated with enamel is subjected to the acid vapors the enamel will decompose, forming a white deposit, and when attempts are made to dip such ware for a second application of enamel it will be found very difficult to get a uniform coat of enamel over the surface.

A useful expedient adopted at some plants is to cover the surface of the acid with a film of flour, bran, or other similar ground mill product. It has been found that by sprinkling a few handfuls of wheat flour over the tank daily, practically all inconvenience from acid vapor is eliminated. These organic substances, due to their charring by the acid, form a blanket of charcoal and foam over the acid, which retards the expulsion of the hydrogen gas and acid fumes. It is claimed by manufacturers of some of these compounds that the retention of the hydrogen gas in the bath accelerates pickling, but experience of those using these materials apparently shows the contrary to be true. In a number of cases the use of these materials has been discontinued, due to the "killing" of the acids after their use.

(c) **STRENGTH OF THE ACID.**—The subject of strength of acid necessary to give the highest efficiency has been studied by several investigators. The work of Grünwald⁴ in this connection is worthy of note. He found that HCl at 17° Baumé gave maximum speed when cold, and at 22° Baumé gave maximum speed

⁴ Grünwald, J., *Technology of Iron Enameling and Tinning*.

when heated to 60° C. He concludes that sulphuric acid is superior to hydrochloric because it can be produced at higher concentration, sulphuric being obtainable at 60 to 66° Baumé, while the maximum concentration for hydrochloric is 24° Baumé. He names 60° C as the temperature at which the highest efficiency is obtained in pickling.

(d) ABSORPTION OF GASES IN PICKLING.—Treischel ⁵ has shown that the amount of blistering encountered in enameling sheet steel can be greatly reduced by the substitution of sand blasting or of pickling with 3 per cent acid solutions for pickling with 10 per cent acid solutions. He attributes the blistering to the absorption of hydrogen by the steel during pickling in strong acid solutions.

(e) MANIPULATION OF THE PICKLING OPERATION.—Ware should be carefully placed in the pickling acid so as to prevent pockets of air being entrapped in corners and so as to avoid the contact of flat surfaces with each other. It is important that the pickling operation be not prolonged unnecessarily, since this not only results in waste of acid but also reduces the thickness of the metal. When it is found that a spot on a piece of ware has not been thoroughly pickled because of a pocket of air or because two flat pieces have been in contact with each other, a repickling, for about the same length of time as the original article required, is necessary. This results in a loss of acid and variation in structure of the surface which may prevent the enamel from adhering properly.

The general practice in enameling plants is simply to place the ware in the acid and allow it to remain there until pickled. Sometimes the operation requires 30 to 40 minutes. This is bad practice from every point of view. It results in loss of time, loss of acid, and a lack of uniformity of structure in different parts of the surface. In steel-plant practice the metal is continually agitated by a mechanical device during the pickling operation, and it would be decidedly to the advantage of enameled-ware manufacturers if they adopted a similar practice. The agitation of the bath insures a very much higher efficiency in the pickling operation than is possible to obtain when the ware is merely left quiet in the acid. This can be accomplished either by moving the ware by a mechanical device such as is in general use in steel plants or by agitating the solution itself. Agitation not only accelerates the

⁵ Treischel, Chester, The Cause and Control of Blistering in Sheet-Steel Enameling, Jour. Am. Ceram. Soc., 2, 774.

rate of chemical action, but, what is still more important, it accelerates the mechanical action of removing the scale.

The removal of scale from a sheet of steel in pickling is very largely a mechanical action. The amount of scale taken into solution during the operation is very small, by far the larger percentage being removed by the acid penetrating beneath the scale and dissolving the surface layer of steel. During the pickling operation many flakes of scale can be seen floating in the solution, and a sludge consisting of iron scale very soon collects on the bottom of the tank. Of course, the acid continues to act upon the scale after its removal from the steel, but this is the case with only strong acid solutions and not with weak solutions. The higher form of iron oxide, Fe_2O_3 , is more easily acted on by the acid than are the ferrous oxides, Fe_3O_4 and FeO .

The loss of acid due to unnecessary action on the sludge which settles to the bottom of the tank has been considered of sufficient importance by some to justify employing a method for its removal from time to time. Grünwald ⁶ mentions a method proposed by Cowper-Cole, which consists in electrolytic separation. He suggests decantation of the solution as being simpler. It seems doubtful if this loss will justify the separation by either means. There certainly will be no saving if the solution is in continual use, because the amount of scale deposited from a single batch of ware is sufficient to thoroughly contaminate the solution. If, however, the acid is to be allowed to stand for some time it should be decanted into clean carboys or a clean tank, thereby preserving its strength for use when needed.

(f) **ELECTRIC PICKLING**—The electric pickling process consists in passing an electric current through the acid during pickling, using the iron to be pickled as the cathode. It offers some advantages over ordinary chemical pickling and has long been advocated as a cheaper process, but it has not been extensively adopted as yet even by steel manufacturers. Some advantages of the process are: (1) It uses less acid per unit area of iron pickled. (2) It is a far more rapid process than ordinary pickling. This difference becomes greater as the amount of scale to be removed increases. (3) Electric pickling in cold acid takes about the same time as ordinary pickling in hot acid. This makes it possible to avoid the injurious effect of hot acid vapors on workmen and machinery.

⁶ Grünwald, J., *Technology of Iron Enameling and Tinning*.

(g) **WASHING AFTER PICKLING.**—When steel is properly pickled no scrubbing will be necessary to remove the scale. The practice of scrubbing ware in water after taking from the acid bath should be condemned in all cases. While scrubbing will not hurt a piece of properly pickled steel, provided it is done under water, the fact that it needs such treatment is an indication that it is not properly pickled. If the acid has not loosened the scale from the steel so that ordinary rinsing in water will wash it off, it will be very imperfectly removed by scrubbing with a brush or sand. Objection to scrubbing also arises from the fact that workmen will not keep the ware under water during the operation, and steel wet with water containing traces of acid rusts very rapidly. Consequently, portions of the ware which come in contact with the air during the scrubbing operation become coated with a film of iron rust, which is very detrimental to the future enameling operations. The proper procedure, in case a piece of ware comes from the pickling tank with scale still adhering which would require scrubbing to remove it, is to replace it in the pickling tank and allow the acid to remove it.

An ample supply of clean running water should be available for washing the ware after it comes from the pickling bath. If the ware is thoroughly washed in water, practically all acid can be removed. In making any but one-coat ware, however, it is not good practice to dispense entirely with the soda bath which ordinarily follows the bath in fresh water. Even with the most thorough washing in water it is impossible to prevent some of the acid going over to the next tank, and a very small amount of acid left on a piece of steel will cause rusting which will give serious trouble when the first coat of cover enamel is burned. Therefore, after washing the ware in clean water it should be immersed in a boiling solution containing a small amount of alkali. The solution should not be strongly alkaline, because upon drying the alkali will crystallize and be deposited in large amounts in corners and at points where the solution runs when the ware is set up to dry. The deposit will decompose when the first coat of enamel is burned and is liable to cause a defective piece of ware. It should be sufficiently alkaline to give a distinct reaction with litmus paper and should be frequently tested and fresh alkali added when required. It is better to add a little soda ash three or four times a day than to add a larger amount to the solution at one time.

The steel as it comes from the boiling soda solution will usually contain sufficient heat to insure rapid drying, but to prevent rusting it should be placed in a drier and dried almost instantly.

(h) **APPEARANCE OF PICKLED STEEL.**—It is generally supposed that steel which has been perfectly pickled should present a perfectly clean, bright surface similar to that obtained by scratching with a file or by sand blasting. The impression is erroneous, however, and may lead to trouble. A piece of steel which comes from the pickling room with a clean appearance should be looked upon by the enameler with suspicion as an indication that the soda bath is very weak and the acid is probably not all neutralized. When the steel enters the soda bath it is coated with a solution of ferric chloride, and if the soda solution is sufficiently active there will be formed a precipitate of ferric hydroxide, which floats in the soda solution. When the ware is taken out, a film of the hydroxide will be left on the surface and will impart a brown color to the ware when dry. This dirty brown color, therefore, is an indication that the ware is free from acid or rust resulting from unneutralized acid.

III. RAW MATERIALS FOR ENAMELS

The raw materials ordinarily used in the making of enamels for sheet iron are the following:

Silica:	Sodium and potassium salts
Sand	Compounds of antimony
Ground quartz	Bone ash
Feldspar	Manganese dioxide
Borax	Cobalt oxide
Cryolite (natural and artificial)	Nickel oxide
Fluorspar	Copper oxide
Barium carbonate	Clay
Zinc oxide	Tin oxide

1. SILICA

All enamels may be considered as silicates or borosilicates. Hence in enamels, as in most glasses, silica (SiO_2) may be regarded as the fundamental ingredient. In enamels it is derived chiefly from flint, quartz, and feldspar.

Flint is hard opaque material of a specific gravity ranging from 1.9 to 2.3, usually more or less colored by impurities. It consists mainly of silica in the amorphous form, partially hydrated, but usually contains some crystalline silica. In many of the deposits in the United States the material contains considerable iron oxide, which renders it unfit for use in white enamels. There are deposits in the South which could probably be used satisfactorily, as the

silica in these is almost entirely amorphous, and the material burns to a pure white color. English and French flint are imported and used to some extent.

Quartz is the most common crystalline variety of silica. It is very abundant and is found in a high degree of purity in quartzites and white sandstones. It is hard, is transparent when pure, and has a specific gravity of 2.66. Pure grades of quartz are ground and furnished to the enameler in powdered form. The term "flint" is frequently applied to ground quartz, but the two materials should be distinguished.

Sand is identical with quartz in chemical and physical properties, and is also obtainable in a quite pure state.

While the pottery industry has long recognized a very material difference in the results obtained by the use of quartz and flint in both bodies and glazes, this difference has not been generally recognized by enamellers. It is usually supposed that the form in which the silica is added to the enamel is unimportant, since it is all thoroughly melted to a glass in the smelter, and the final product is the same if all the silica is taken into solution. The form of the silica, however, in both ground-coat or white enamels, should be considered. It should be remembered that the enameler has incorporated in his melt certain materials which will perform their function only in case the smelting is stopped at the right time. This is especially true of white enamels, but to some degree also of ground coats. One of the chief differences in the three forms of silica mentioned is in the rates at which they combine with or dissolve in other materials during the melting of the batch. Amorphous flint, if ground to equal fineness, combines more readily than powdered quartz, while the coarser sand grains combine less readily than either. It follows, therefore, that the time and the temperature required for melting are materially affected by both the condition and the fineness of the silica. These variations in melting conditions, in turn, have a decided effect upon the enamels in respect to those ingredients which may lose their value through excessive heat treatment in the smelter. Thus, cryolite, antimony oxide, and tin oxide give their maximum value as opacifiers with minimum heat treatment in the smelter. The form and fineness of the silica should therefore be carefully watched and allowed for in compounding the batch.

All these forms of silica may be used with good results, but experience has shown that in the same enamel a smaller quantity

of sand than of powdered quartz should be used. Similarly, less quartz than flint should be used, but the difference in this case is less than in the former. Flint is likely to carry a high percentage of moisture, especially when just received. This should be regularly determined and allowed for in the batch.

2. FELDSPAR

From a mineralogical standpoint feldspars may be divided into three classes:

1. Potash feldspar, including orthoclase and microcline; composition, KAlSi_3O_8 or $\text{K}_2\text{O}, \text{Al}_2\text{O}_3, 6\text{SiO}_2$; specific gravity, 2.54 to 2.56.

2. Soda feldspar, albite; composition, $\text{NaAlSi}_3\text{O}_8$ or $\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 6\text{SiO}_2$; specific gravity, 2.605.

3. Lime feldspar, anorthite; composition, $\text{CaAl}_2\text{Si}_2\text{O}_8$ or $\text{CaO}, \text{Al}_2\text{O}_3, 2\text{SiO}_2$; specific gravity, 2.765.

In addition there are various mixtures of these varieties—anorthoclase, which consists of equal parts of potash feldspar and soda feldspar, and the soda-lime or plagioclase feldspars, which vary in composition from 6 parts of soda feldspar and 1 part of lime feldspar, to 1 part of soda feldspar and 6 parts of lime feldspar. As obtained for commercial purposes the materials are never pure, but contain more or less of a mixture of the different varieties, as well as excess silica and other minerals.

Information relative to feldspar deposits and the composition and properties of the materials may be found in references cited below.⁷ Analyses of some commercial feldspars given by Bastin⁸ are shown in the accompanying table.

TABLE 1.—Analyses of Some Commercial Feldspars

	(a)	(b)	(c)	(d)	(e)	(f)
SiO_2	64.7	64.98	66.23	65.95	76.37	65.87
Al_2O_3	18.4	19.18	18.77	18.00	13.87	19.10
Fe_2O_333	Trace	.12		
CaO		Trace	.31	1.05	.26	.20
MgO25	None	Trace	None	None
K_2O	16.0	12.79	12.09	12.13	5.24	12.24
Na_2O		2.32	3.11	2.11	3.74	2.56
H_2O30	.64
Loss on ignition48				
	99.1	100.33	100.51	99.36	99.78	100.61

⁷ Watts, A. S., Bull. 53 and 93, U. S. Bur. of Mines; Bastin, E. S., Bull. 420 and 445, U. S. Geol. Survey, De Schmidt, H. S., Bull. 401, Canada Department of Mines; Galpin, S. L., Bull. 30, Georgia Geol. Survey.

⁸ Loc. cit.

The mineral deposits from which most commercial feldspar is obtained are called pegmatite. This term includes deposits varying in composition from nearly pure feldspar with a little quartz as impurity to a mixture containing a little feldspar with a large amount of other minerals.

Pegmatites are coarsely crystalline granites in which feldspar and quartz are the chief constituents. The other constituents of the granite in which the pegmatite is an intrusion may be totally absent or replaced by rare minerals. Sometimes the constituents of these dykes of pegmatite are separated into distinct bands in such a manner as to make it possible to obtain feldspar in commercial quantities absolutely free from other minerals, but in most cases the feldspar and quartz are too intimately associated to admit of any such possibility. In mining such material, the undesirable minerals which are sufficiently coarsely crystalline to be distinguished are sorted out, and the resulting product of the mine is necessarily a feldspar containing more or less quartz and other minerals.

Certain ceramic industries, notably the pottery industry, have insisted upon getting pure feldspar, and the producers of this material have attempted to supply the demand; as a result, there are on the market three grades of feldspar, termed "grades 1, 2, and 3," according to the purity of the material.

Referring to the demand for pure feldspar, A. S. Watts⁹ makes the following statements:

That the present demand for a pure feldspar in many of the industries is unwarranted is evidenced by the practice both in England and throughout continental Europe.

The enormous white-ware industries of Staffordshire, England, are dependent upon the coarse granites or pegmatites of Cornwall for their feldspathic material. This district does not produce any pure feldspar, but only material which is a mixture of feldspar and quartz, with minor amounts of other materials. The success which has attended the use of this material is indicated by the fact that enormous quantities of crude Cornwall stone are annually imported into the United States for manufacturers who find it more satisfactory for their purpose than any of the American feldspars.

In France the supply of feldspar is limited, indeed, and the famous wares of Limoges are to-day made from the semi-weathered pegmatites of the St. Yrieix district. These are crushed and pulverized by wet grinding, and to them are added what additional kaolin and flint are necessary to produce the desired strength for molding and the demanded translucency when fired. The feldspars of Scandinavia are in reality pegmatite, if one may judge from the analyses obtainable.

The foregoing indicates that deposits of pure feldspar are no longer available for use of the European manufacturer, and he has found it possible to produce an equally satisfactory ware from a mixture of feldspar and such other impurities as are not actually injurious when the material is properly prepared.

Toward this same condition the American user of feldspar is rapidly approaching, and conditions are not improved by ignorance of the gradual change that is occurring

⁹ Watts, A. S., Bull. 92, U. S. Bur. of Mines; 1916.

or by imagining that the same quality of material is being used as when the deposits were first opened.

The aim of the foregoing statements on feldspar is to show: (1) that there are several different kinds of feldspar, each having characteristic properties of its own; (2) that the nature of the deposits from which feldspar is obtained precludes the possibility of obtaining in large amounts pure feldspar of any one kind; (3) that feldspar with quartz (SiO_2) as the only impurity in appreciable amounts is readily obtainable, but that the ratio of feldspar to quartz even in the same deposit varies widely; (4) that pure feldspar is not a necessity to obtain good results, provided the impurities are not themselves detrimental to the ware in which they are incorporated.

While this last statement was intended to apply to white-ware bodies, it can certainly be correctly applied to feldspar for sheet-iron enamel purposes. There is no limit to the degree in which feldspar and flint can vary in the enamel mixture, provided the fluxing elements of the feldspar are supplied from other sources when the feldspar is replaced by flint. In discussing European enameling practice, Grünwald¹⁰ gives the following table showing the ratios of feldspar to quartz in the raw mixtures for enamels:

Ground coat	Common white	Soft white	Acid-proof white	White for cast iron	Powdered white	Blue
25:21	15:30	25:9	6:47	39:0	26:0	29:18
26:18	21:19	13:36	31:19	34:26
28:16	20:28	17:40	26:13	38:23
31:20	27:14	42:0	40:0
40:1	30:8	46:0	57:8
40:3	34:19
.....	39:0

While the table indicates wide limits of variation, it will be noted that in all cases some feldspar is used, and in nearly all cases the feldspar exceeds the flint.

A number of formulas which have been successfully used in America show the following ratios between feldspar and quartz:

Ground coat	Common white	Acid-proof white	White for cast iron	Blue
1.6:1	1.3:1	0:1	2:1	0.90:1
1.0:1	1.1:1	.1	1:1	1.0:1
1.1:1	.9:1	1:1	1:0	.70:1
.9:1	.9:1
.9:1	.75:1
1.0:1

It will be seen that American practice differs slightly from European in that the feldspar content is frequently less than the flint and the ratio generally runs close to 1:1.

¹⁰ Grünwald, J., Raw Materials of the Enameling Industry, Trans. by H. H. Hodgson, Griffin; 1914.

The basis of all enamels is SiO_2 , and, as was said in discussing silica, the nature of the enamel is materially influenced by the source from which the silica is obtained. While in compounding sheet-iron enamels the chief source of silica is flint or quartz, still a large amount of silica is added in the form of feldspar, not only as impurity in the feldspar, but as part of the mineral itself. As is indicated by the chemical composition of feldspar, every 100 pounds of it incorporated in the enamel carries with it about 65 pounds of SiO_2 . While it is not impossible to replace a part or all of the feldspar of the enamel with flint, soda, niter, and clay, as is indicated by the ratios given above, it is not possible to obtain enamels of the same physical properties by replacing feldspar with chemically equivalent proportions of other materials. The reason for this is much the same as was noted in discussing the effects of silica from different sources.

Potash feldspar melts at temperatures not far from 1200°C , which is generally well below the temperature of the smelter in melting enamels. In contact with the other materials in an enamel batch it melts at still lower temperatures. Silica in the form of flint, ground quartz, or sand never melts at the smelter temperature, but must be taken into solution by the action of the other materials which are melted in the batch. Therefore the feldspar in the batch becomes an active flux at comparatively low temperatures, thereby accelerating the formation of a homogeneous glass from the components of the batch, while a synthetic mixture of materials giving the same resulting product as the feldspar would contain silica and clay, both of which would retard the melting operation. It would also contain an alkali which melts more readily than the feldspar itself and which is a much more active flux than feldspar. While this vigorous action of the alkali tends to overcome the loss in fusibility of the batch resulting from the extra flint and clay, it at the same time reacts upon those ingredients of the batch which it is desired to keep from solution and decomposition. The result is that, while the fusibility of the enamel is not greatly decreased by substituting other materials for feldspar, the extra time required for melting, together with more vigorous action on the opacifying agents, tends to destroy the opacity of the resulting enamel. Thus, experience has shown that feldspar enamels are more opaque than enamels of the same chemical composition made without feldspar or with a low content of feldspar.

3. BORAX

(a) PREPARATION.—Anhydrous boric acid (B_2O_3), like silica (SiO_2), is one of the essential constituents of every enamel, with the possible exception of acid-proof enamels for special purposes. While it is possible to make a silicate containing no B_2O_3 of sufficiently low fusing point to use as an enamel, it is very seldom done in enamels for steel and iron because there is no economic gain, and such an enamel is very difficult to apply to these metals.

Many minerals containing boric acid occur in nature, most important of which are the following: Colemanite, $2CaO_3B_2O_3 \cdot 5H_2O$; borocalcite, $CaO_2B_2O_3 \cdot 6H_2O$; tincal, $Na_2O_2B_2O_3 \cdot 10H_2O$; boronatrocalcite, $Na_2O_2CaO_5B_2O_3 \cdot 10H_2O$; boracite, $6MgOMgCl_2 \cdot 8B_2O_3$; boric acid, $B_2O_3 \cdot 3H_2O$.

Borax, a hydrated borate of sodium corresponding in composition to the mineral tincal, is the source of the B_2O_3 most commonly used in enamels. It is obtained by refining the natural mineral, colemanite. The process of manufacture increases the cost of B_2O_3 very considerably as compared to the cost if the natural minerals are used. Colemanite can be readily freed from impurities by calcination and screening, and serves as an excellent source of B_2O_3 for enamels. In fact it is in many respects much better than borax, and it would seem that the enamelers could advantageously make some arrangement with the producers of borax whereby this mineral might be obtained for their use with a material reduction in cost compared to that of borax.

What has been said of colemanite is also true of boronatrocalcite. While the substitution of either of these minerals for borax necessitates some readjustment of the enamel formula, a considerable saving in cost is possible. This is due not only to the lower cost of the B_2O_3 , but to the fact that it is possible to produce white enamels with smaller amounts of opacifier (tin-oxide and antimony compounds) when these are used than when borax is used. Borax reduces the effectiveness of the opacifiers by partially taking them into solution during the melting of the enamel, while colemanite and boronatrocalcite are decidedly less active in this respect and do not so seriously affect the opacity of the enamel.

Experiments have been performed to determine the possibility of replacing borax with other minerals containing B_2O_3 , and the results obtained were entirely satisfactory. White enamels were melted in which colemanite and boronatrocalcite were used to

introduce the B_2O_3 , and the Na_2O of the borax was replaced with soda ash, the CaO introduced in the colemanite being allowed for by reducing the fluorspar. Enamels of the same ultimate chemical formula were melted side by side, one containing borax, one containing boronatrocalcite, and one containing colemanite. The one containing colemanite was somewhat harder to melt than the others. No difference was noted in the fusibility of those containing borax and boronatrocalcite. When these enamels were applied to iron, the ware made from the colemanite and boronatrocalcite enamels had decidedly the best texture and purest white color.

Colemanite occurs in large quantities in California. Boronatrocalcite occurs in Nevada, Peru, Argentina, Chile, South Africa, and Nova Scotia. Boracite is the chief source of the borax industry in Europe, occurring in considerable quantities near Stassfurt and also near Westergehn (Saxony).

Boracic acid is found in many volcanic regions, the most important deposits being in Tuscany. The crude acid, called Tuscany acid, which is collected in artificial lagoons, is contaminated with sulphate salts, etc., and is colored yellowish brown. It contains about 82.5 per cent boric acid, and can be refined by dissolving in hot water and mixing the solution with freshly ignited powdered charcoal, which removes the coloring matter. The clear solution, upon evaporation, leaves the refined boracic acid of commerce.

Boric acid is not used to any great extent in enamels. It is more expensive as a source of B_2O_3 than borax, but it acts similarly to colemanite and boronatrocalcite in not decreasing the efficiency of the opacifying agents. It is also claimed that boric acid is a desirable source of B_2O_3 in the production of colored enamels, because the pigments produce cleaner and stronger colors than when borax alone is used.

Regardless of what raw material is used as a source of B_2O_3 , it is highly essential that it be in a finely divided condition and thoroughly mixed with the batch. There are three forms of borax in use by the enameling trade—powdered, granulated, and crystals. The powdered form is most desirable and will give best results, provided precaution is taken to grind all lumps, and the moisture content is regularly determined. Granulated borax is more commonly used than either of the other forms. It comes in sacks of 100 pounds each, which are convenient to handle.

In general, it is probable that more uniform results can be obtained by its use, because powdered borax always becomes lumpy by absorption of moisture, and these lumps will not always be crushed before mixing in the batch. On the other hand, the crystal borax which comes in large lumps from one-fourth to 1 inch in diameter should never be used. Where borax in this form is used in the enamel, thorough mixing is impossible, and while these lumps melt readily upon being subjected to the heat of the smelter, they immediately take into solution whatever is in immediate contact with them, while other portions of the batch remain unaffected for a long period because of lack of a proper portion of fluxing material.

Borax requires a close watch on its moisture content. It is deliquescent, and its moisture content varies somewhat with the condition of the atmosphere in which it is stored. It is of especial importance that every new consignment of borax received be tested to determine the amount of moisture it contains. The water content of borax is also influenced largely by the condition under which it is precipitated; thus two distinct crystalline forms are obtained of the formulas, $\text{Na}_2\text{O}, 2\text{B}_2\text{O}_3, 10\text{H}_2\text{O}$ and $\text{Na}_2\text{O}, 2\text{B}_2\text{O}_3, 5\text{H}_2\text{O}$. The compositions of these two forms of borax are as follows:

	1	2
Na_2O	16.26	22.6
B_2O_3	36.59	47.9
H_2O	47.15	30.8

The pentahydrate, containing 5 molecules of water, is found when a saturated solution is allowed to crystallize above 62°C ., while that with 10 molecules of water is precipitated from solution below 62°C . Since there is a possibility of these two crystalline forms being present in almost any proportion, it will be readily seen that the enameler has no idea of how much anhydrous borax he is incorporating with his batch unless he knows how much water his material contains. It should be stated, however, that there is little probability of a manufacturer shipping common borax, decahydrate borax, containing any large amount of the pentahydrate; it would be decidedly to his financial disadvantage to do so, and it is a simple matter to avoid the formation of the pentahydrate when the decahydrate is being made.

The most simple method of determining the water content of borax is to weigh a definite amount, melt carefully to a glass,

avoiding any loss, and then weigh the glass after cooling in a desiccator. The loss in weight, divided by the original weight and multiplied by 100, gives the percentage of water in the original material.

(b) FUNCTION OF BORAX IN ENAMELS.—Borax is used in enamels for its fluxing action, being one of the most active in this respect of all the materials used in the enamel batch. It melts readily and attacks vigorously the other ingredients of the batch, thus accelerating the rate at which the enamel is brought to a uniform molten state. Owing to the high cost of borax and its effect in taking into solution the opacifiers, thereby reducing their efficiency, it is advisable to use as little of it as possible. It is not only valuable as a flux in melting the frit, but it also imparts to the resulting enamel the property of easy fusibility, which is essential. However, this property can be largely controlled by proper adjustment of the ratios between the other ingredients of the batch. Borax also imparts a high luster to enamels, which is more essential in some kinds of ware than in others, but this also can be greatly modified by varying the ratio between the silica and the other ingredients. One of the undesirable properties imparted to enamels by borax is susceptibility to corrosive action. Other things being equal, the solubility of enamels is directly proportional to the B_2O_3 content.

Grünwald¹¹ gives the following table showing the percentage of borax used in raw mixtures of enamels:

	Per cent
Ground for sheet iron.....	30-45, usually 35-39
White for sheet iron.....	20-34, usually 24-27
Blue for sheet iron.....	18-29, usually 23-29
Acid proof for sheet iron.....	13-23, usually 24-29
White for pottery.....	21-41, usually 34-40

In American practice the borax content runs from nothing in some acid-proof enamels up to 40 per cent in soft white enamels. The tendency is to use too much borax because it is easy to get an easily fusible enamel of high gloss with a high borax content.

4. CRYOLITE

This highly important constituent of enamels is a double fluoride of sodium and aluminum. It functions in the enamel both as a flux and an opacifier. Its chemical formula may be written Na_3AlF_6 or $3 NaF, AlF_3$. It is composed of 32.85 per cent

¹¹ Grünwald, J., *Raw Materials for the Enamel Industry*, p. 69, Griffin; 1914.

sodium, 12.85 per cent aluminum, 54.50 per cent fluorine, or 60 per cent sodium fluoride plus 40 per cent aluminum fluoride.

The only known natural deposit of any extent occurs in southern Greenland, from which source all of the natural cryolite in use is obtained. Many brands of artificial cryolite are on the market, some being more nearly pure than that obtained from Greenland. As a rule, the only impurity contained in the natural cryolite is silica, and, if the amount of this is known, the use of cryolite containing it in considerable quantities should cause no serious trouble. It is, however, bad policy to pay the price usually prevailing for cryolite for a brand containing a very large amount of silica, since this can be bought as quartz for very much less than as cryolite. There is no advantage in the natural over the artificial cryolite, provided the chemical composition is the same. However, a few unscrupulous dealers have sold all sorts of concoctions with fantastic names, purporting to be artificial cryolite. Artificial cryolites have been sold containing from 5 to 30 per cent silica. The result is that all artificial cryolite is in bad repute in some quarters.

The mineral, sodium aluminum fluoride, can be made by digesting aluminum hydroxide ($\text{Al}_2(\text{OH})_6$) with sodium fluoride, or by precipitating it with common salt when hydrated alumina is dissolved in hydrofluoric acid. The artificial mineral can be made free from impurities, and when so made exhibits all the properties of the natural mineral.

Cryolite melts to a white enamel-like mass at about 1000°C and has a specific gravity of about 2.95. When used in enamel in amounts from 5 to 10 per cent it is an efficient opacifier. It is not good policy to use less than 5 per cent; practically no opacity will be obtained, and its fluxing value in small amounts does not justify its high cost. It is not advisable to use more than 18 per cent, since in larger quantities it tends to destroy the luster of the enamel and to increase its liability to destruction by corrosion.

Much has been written on the subject of fluorides as opacifiers, and many theories have been advanced as to the agent producing this opacity. For discussion on this subject the reader is referred to Staley.¹² All fluorides have the property of imparting some degree of opacity to enamels if the heat treatment is not too severe and the amount of fluoride present is sufficient, but cryolite is the one most generally used and probably the most efficient.

¹² Staley, H. F., B. S., Technologic Paper, No. 142, p. 46.

5. FLUORSPAR

Fluorspar (CaF_2) or calcium fluoride is composed of 51.3 per cent calcium and 48.7 per cent fluorine. It has a specific gravity of 3.1 to 3.2, and melts at 1400°C . It is an active flux and in large amounts acts as an opacifier. It is distinguished from other lime compounds in that it generally, although not always, reduces the melting point of the enamel.

Lime in some form is desirable in the production of enamels, unless lead is present. Enamels containing no lime are very difficult to smelt and are likely to froth and boil when burned on the ware. A very small amount of lime (1 to 2 per cent) is sufficient to overcome this tendency. When the lime in the batch is low, 4 per cent or less, it is quite unimportant whether it is added as fluorspar or as whiting, but when large amounts are used, fluorspar is the most desirable source because it makes the enamel smelt more easily. The fusibility of the finished enamel will be practically the same if the smelting is thorough, regardless of whether fluorspar or whiting is used.

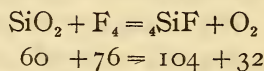
Fluorspar has a very injurious effect on the color of enamels in which antimony oxide is the opacifier, imparting a bluish-green color. While the color of enamels for steel is not generally of great importance, for some purposes a cream or pinkish white is desired rather than blue white. In such cases the fluorspar content of the enamel is of great importance. Enamelers have tried for years to replace tin oxide with antimony oxide and have experienced difficulty in getting the desired color from antimony oxide. The reason for this difficulty has been largely due to the high fluorspar content of the enamels, which gives a correspondingly high fluorine content. The accuracy of this statement can be demonstrated by comparing the color of two enamels containing antimony oxide, using fluorspar in one and in the other replacing the fluorspar by calcium carbonate in the ratio of 100 parts calcium carbonate to 78 parts fluorspar. The one made from calcium carbonate will be cream to yellow, depending on the antimony oxide used, the percentage of calcium and of other ingredients of the batch, while the one made with fluorspar will be blue white to a dirty green.

An enamel containing more than 3 per cent of fluoride will be decidedly weakened in its ability to resist the solvent action of acids, alkalies, or water. This factor is, of course, largely affected by the intensity of the heat treatment during fritting. If the smelting oper-

ation is sufficiently intense to drive off all of the fluorine, then the above statement will not hold, but experience has shown that in the ordinary smelting operation this point is not always reached. The nature of the enamel, its viscosity, and the raw materials used influence this point very materially.

During the smelting the fluorspar decomposes to some extent with liberation of fluorine and combination of the calcium with silica and boric acid. Our knowledge of the reactions in melts as complex as those of enamels is too limited to determine what compounds are actually formed. Such studies as have been made of silicate systems show that the products vary with the heat treatment and the proportions of the different ingredients present. Even where lime and silica only are present, several compounds may be formed. The difficulty of determining what takes place in enamel melts is much greater by reason of the greater number of materials entering into the reactions.

The fact that fluorspar lowers the fusion point of enamels more than an equivalent amount of calcium carbonate does indicate that it is either not completely decomposed or that the fluorine recombines in some form in which it can act as a flux. If the fluorine from the fluorspar is all driven out of the enamel, the compound resulting is probably not materially different from what is obtained when calcium carbonate is used as the source of lime. It is also important to note that the loss of silica from an ordinary enamel would be almost negligible even if all of the fluorine were liberated as SiF_4 , since an enamel seldom contains more than 8 per cent fluorspar. This gives approximately 4 pounds of fluorine to combine with silicon as follows:



76 pounds fluorine require 60 pounds silica.

4 pounds fluorine require $\frac{60}{76} = 3.15$ pounds silica.

Thus the silica would be reduced only about 3 per cent in the enamel. While this would be a decided loss in silica, it would hardly be sufficient to make very material difference in the fusibility or in the resistance to corrosion.

It remains, therefore, a matter of conjecture as to the manner in which fluorine is liberated. The tendency of fluorine to combine with silica to form silicon fluoride makes it seem highly probable that the fluorine would come off as SiF_4 rather than in

the free state. However, while from a scientific viewpoint this is a very interesting question, the matter in which the enamel manufacturer is chiefly interested is the way in which the fluorides affect his enamel. While the determination of the actual facts would without doubt enable enamellers to more accurately control their products, they can profit greatly by a careful and systematic study of mixtures containing fluorides, even though the exact facts remain unknown.

6. BARIUM CARBONATE

Barium carbonate is found in nature as the mineral witherite. It has the chemical formula BaCO_3 and belongs to the group known as alkaline earths. The barium carbonate used in enamels is not the natural mineral, but artificially precipitated barium carbonate. It is only within recent years that it has found extensive use in enamels. Its use was brought about by the attempt to eliminate lead from enamels while at the same time maintaining the property of easy fusibility.

Barium carbonate in enamels acts similarly to calcium carbonate in some respects, while in others it resembles lead compounds. It decomposes with great difficulty, and for this reason enamels containing it are difficult to smelt. It is even less active as a flux in the smelter than calcium carbonate, but having been properly smelted it imparts to the enamel the property of easy fusibility, being almost equal to lead oxide in this respect. It is much cheaper than lead oxide and is decidedly less poisonous than lead compounds. It offers a means of producing enamels having the desirable properties of high luster, density, and easy fusibility of lead enamels without the dangers of poisoning attending their use.

In using barium carbonate, care must be taken to obtain a grade free from barium sulphate. Barium sulphate is injurious to enamels, destroying their luster and frequently causing blisters in white enamels.

7. ZINC OXIDE

Zinc oxide is closely related to tin oxide in its chemical nature. It is used very extensively in making some types of glazes, notably Bristol glazes for stoneware. In these glazes zinc in connection with alumina is the chief opacifying agent. It is an active flux when used in small amounts, but an excess of it produces infusibility. While it is an efficient opacifier in pure silicate glazes, it has practically no opacifying power when fritted in borosilicate enamels.

It is used quite extensively in making enamels, chiefly for its fluxing power and its property of increasing the stability of enamels against corrosion. It is very similar to barium in the effect it has on enamels. It is less active than barium in reducing the melting point, but it produces somewhat more stable enamels. Used in small amounts it gives enamels with high luster, but excess destroys the luster. It is bad practice to add raw zinc oxide in the mill. It is not efficient as an opacifier when thus used, and it destroys the luster and imparts a bad color to the enamel.

8. SODIUM AND POTASSIUM SALTS

Soda ash is the form in which soda is commonly introduced into enamels, except that brought in by borax and cryolite. It is anhydrous sodium carbonate (Na_2CO_3), composed of 58.5 per cent Na_2O and 41.5 per cent CO_2 , and is to be distinguished from the crystalline or hydrated sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$). The water in the latter material may be expelled by heating to 100°C . The anhydrous sodium carbonate is also known as 58 per cent soda ash. It is a very active flux in enamels.

All enamels contain some sodium oxide, derived chiefly from borax, cryolite, and soda ash. The fusibility and liability to corrosion are increased with increase of Na_2O and K_2O . These two oxides seem to be interchangeable in enamels without any very material difference being noted in the results. There is an opinion prevailing that potash gives a little more luster and strength to enamels than soda, but no data is available to substantiate this claim. The carbonate of potash has the disadvantage of being more expensive than soda, and because of its hygroscopic nature it is troublesome to handle. It is therefore seldom used in enamels.

Most enamels contain some oxidizing agent in the form of either potassium or sodium nitrate. Sodium nitrate is generally used because it is the cheapest. Only a small amount of nitrate is necessary, 2 to 4 per cent being sufficient to maintain oxidizing conditions in most smelting operations. It is highly important that sufficient niter be present to prevent reduction of any easily reducible compound in the batch, especially lead or antimony compounds. The color of the resulting enamel is very materially affected by slight reduction, which may be caused by a smoky flame or by carbonaceous compounds incorporated in the batch. It is of especial importance that enamels containing antimony oxide have sufficient oxidizing agent. Reduction of such an

enamel not only causes the antimony to go into solution, thereby losing its opacifying power, but it destroys the color of the enamel. Commercial materials always contain some impurities, and there is generally a sufficient amount of iron compounds in the materials to affect the color. This effect will be much more pronounced if the batch is not kept oxidizing during smelting. When the batch is thoroughly oxidized, as much as 1 per cent of red oxide of iron can be incorporated in a white enamel without any serious damage to the color, but if the batch is reduced in smelting the color will be very dark and the enamel therefore unsuitable.

For the production of some colored enamels, reducing conditions are desirable, in which case the niter should be left out. Black and dark-blue enamels may be mentioned as cases in point. While these colors can be produced under oxidizing conditions, they will be produced more cheaply and easily under reducing conditions.

The amount of niter in the batch has also an effect on the melting. Enamel without any niter melts with much less frothing than that containing it in sufficient amount to maintain oxidizing conditions. Excess of niter should be avoided, therefore, because it is expensive, because no benefit is derived from using it as a flux rather than some cheaper form of alkali, and because it increases the difficulty of smelting.

9. COMPOUNDS OF ANTIMONY

Antimony, either as the oxide or as some other compound, is one of the principal opacifiers used in making white enamels. In normal times these compounds are much cheaper than tin oxide and when properly used are effective as opacifiers. There are many difficulties attending the use of antimony compounds in enamels, and unless all conditions are right poor results are likely to be obtained.

When heated in the absence of strong acids with bases like sodium, potassium, barium, or lead, antimony oxide functions as a weak acid with formations of antimonates. It is capable of combining with the bases in many different proportions. It is quite a simple matter to form glasses varying from $3\text{RO}\cdot\text{Sb}_2\text{O}_3$ to $\text{RO}_3\cdot\text{Sb}_2\text{O}_3$ by merely mixing the materials and heating. The mixtures melt readily to liquids and can be poured into water and granulated, being quite insoluble in water. They vary in color from a cream to dirty brown, but seldom approach white.

Antimony oxide occurs in three forms: as trioxide, Sb_2O_3 ; tetroxide, Sb_2O_4 ; or pentoxide Sb_2O_5 . The trioxide and pent-

oxide are of a yellow color, while the tetroxide is white. When Sb_2O_3 is heated to 275°C , it is converted to Sb_2O_5 . This, upon being heated to 300°C , is in turn converted to tetroxide, which is the most stable form of the oxide.

Antimony compounds have found extensive uses as opacifier because of certain advantages they possess over the oxide itself. One of these is that the combined antimony, if properly prepared, can be incorporated in ordinary enamels with less modifications of the batch than is necessary when the oxide itself is used. As mentioned before, one of the principal difficulties encountered in using antimony oxide is the control of the color, the antimony affecting the color by combining with different bases forming dark-colored compounds. When the oxide itself is added in the smelter, it combines quite readily, but when it is added in the form of antimonate of some base, it seems to be quite stable, and thus not only has a high efficiency as an opacifying agent but also combines to a smaller extent with formation of undesirable colored compounds.

The results obtainable by using antimony oxide direct depend largely on the quality of the oxide used. The oxide on the market in normal times varies in color from a pure clean white down through a pleasing cream color to a dirty gray. The apparent density of the oxide also varies greatly, depending upon the method of preparation. That prepared by wet chemical processes has a high density—that is, apparent specific gravity—and is generally very clean and white. That deposited from vapor is a light fluffy powder. Better results are obtained with the dense clean white oxide than with the other forms.

Several factors affect the quality of the enamel, and these must be carefully adjusted. If a cream color is desired, the fluorspar content of the enamel must not run above 4 per cent of the raw batch when the antimony oxide is used. Enamels containing fluorspar and antimony oxide have a blue-green color. This color can be largely corrected by additions of cryolite, which acts as an opacifier and masks the blue-green color of the fluorspar-antimony compound. Other fluorides, like sodium fluoride and aluminium fluoride, are not detrimental to the color. Lime in the form of CaCO_3 used in connection with Sb_2O_3 gives good cream colors, but the enamel is more difficult to smelt. The use of sufficient oxidizing agent, niter, is a very important factor in obtaining a good white color.

10. EFFECT OF OTHER CONSTITUENTS OF ENAMEL ON THE COLOR PRODUCED BY ANTIMONY OXIDE

As a basis for this study, the following formula, X, was used:

Potash feldspar	40
Borax	24
Soda ash	6
Sodium nitrate	7
Fluorspar	3
Barium carbonate	5
Zinc oxide	10
Antimony oxide	6

Three different samples of antimony oxide were taken, as follows:

No. 1. Domestic oxide of a dirty gray color, which gave a muddy greenish-yellow color in enamel X.

No. 2. French oxide of a rather strong yellowish color, but which gave fair-colored enamels, tending to a rather strong cream.

No. 3. Best French oxide obtainable, which was of a pure white color and gave a good white enamel.

Samples of each oxide were thoroughly wetted with concentrated nitric acid and immediately roasted to dryness over a hot plate at 110°C , roasting being continued until all fumes ceased to come off and the powder was fine and of uniform color. This roasting converted all of the oxides to a dirty gray color, and when they were mixed in enamel and melted the result was a dirty appearing enamel.

The same oxides were boiled for 30 minutes in concentrated nitric acid. The solution was diluted and filtered and the precipitate was washed free from acid, then calcined at 1000°C . This treatment converted all samples to a clean, cream color, and these, when used in enamel X, gave a clean, cream-colored enamel.

In order to determine the effect of fluorspar in antimony enamels, 50 g batches of the above mixture, leaving out the fluorspar, were weighed up and thoroughly mixed by grinding in a ball mill. Fluorspar was added, as follows:

- | | |
|--------------------------------------|--------------------------------------|
| (a) X with 4 per cent CaF_2 | (d) X with 7 per cent CaF_2 |
| (b) X with 5 per cent CaF_2 | (e) X with 8 per cent CaF_2 |
| (c) X with 6 per cent CaF_2 | (f) X with 9 per cent CaF_2 |

These mixtures were placed in crucibles in a furnace and all melted at once, the enamel poured out, and colors compared. The mixture with 4 per cent CaF_2 gives a fair color with a slight bluish tinge; 5 per cent CaF_2 gives a blue tinge; 6 per cent CaF_2 , a decided

blue; and 8 per cent, more color. The color is distinctly bad with 6 per cent fluorspar.

Lime was then introduced in the enamel in other forms:

- (g) X with 0 CaF_2 + 3 per cent CaCO_3
- (h) X with 0 CaF_2 + 5 per cent CaCO_3
- (i) X with 0 CaF_2 + 7 per cent CaCO_3
- (j) X with 0 CaF_2 + 9 per cent CaCO_3
- (k) X with 0 CaF_2 + 3 per cent Ca(OH)_2
- (l) X with 0 CaF_2 + 5 per cent Ca(OH)_2
- (m) X with 0 CaF_2 + 7 per cent Ca(OH)_2
- (n) X with 0 CaF_2 + 9 per cent Ca(OH)_2

None of these exhibit the blue color, but the opacity is decidedly less with CaCO_3 as the source of lime, and the enamel is more difficult to smelt. The use of Ca(OH)_2 is unsatisfactory as a source of lime, because the enamel froths when melting and is melted to a dense glass only with the greatest difficulty.

Enamels were melted, using different fluorides, as follows:

- (q) X - fluorspar + 3 per cent BaF
- (r) X - fluorspar + 8 per cent BaF
- (s) X - fluorspar + 3 per cent NaF
- (t) X - fluorspar + 8 per cent NaF
- (u) X - fluorspar + 3 per cent cryolite
- (v) X - fluorspar + 8 per cent cryolite
- (w) X - fluorspar + 6 per cent CaCO_3 + 6 per cent cryolite
- (y) X - fluorspar + 8 per cent CaF_2 + 10 per cent cryolite

None of these enamels exhibited the blue color obtained when fluorspar alone is used. These results seem to show that fluorspar, when melted with antimony oxide in enamels of this type is responsible for the objectionable blue color.¹³

Leukonin is an antimony compound, sodium metantimonate ($\text{Na}_2\text{OSb}_2\text{O}_5$), made by roasting antimony oxide with soda compounds the excess of which can be leached out with water, leaving sodium antimonate. This material, as sold, contains from 85 to 97 per cent $\text{Na}_2\text{OSb}_2\text{O}_5$ and other substances as impurities. Leukonin is used successfully in enamels.

IV. PREPARATION OF ENAMELS

1. MIXING THE RAW MATERIALS

General practice in mixing the raw materials consists in weighing the batch, which generally approximates 500 pounds, into a box

¹³ Cf. Staley, H. F., *Trans. Am. Ceram. Soc.*, 17, p. 173.

and then turning the mixture over a few times with a hoe or shovel. In the case of colored enamels it is considered mixed when the coloring oxide is uniformly distributed, imparting a uniform gray color to the batch. In white enamels the practice is to turn the mixture a certain number of times, which is considered to be sufficient. Here is one of the places where enamellers can improve their practice and raise the standard of their ware by doing away with slipshod methods and resorting to more thorough, exact, and economical methods. Rotating drums and other forms of mixing machines give much more satisfactory results.

Every enameler, and even the uneducated laborer who has worked around the smelter, has observed that the enamel smelts more quickly when most thoroughly mixed. This is simply the practical application of the well-known scientific principle that the speed of chemical reactions is directly proportional to the area of surface of contact between the reacting substances. If a fire brick were crushed to a powder and mixed into the batch it would go into solution in the melt and disappear with the other ingredients of the batch, while that same brick when laid in the wall of the smelter will stand for months without being eaten away. This same principle applies to all the refractory ingredients of the batch. A large piece of flint stone will go through a melt and come out with only the sharp edges eaten off. The length of time required for smelting the enamel depends directly upon the fineness of the raw material, especially flint and feldspar, and upon the thoroughness with which they are mixed. It follows, then, that better mixing of the raw materials means less labor, less fuel, less time of smelting, and less wear and tear on the smelter.

It is not only from an economic standpoint that thorough mixing is advisable. The quality of the white enamels is inversely proportional to the length of time spent in producing a thorough melt. Long smelting results in a considerable reduction in opacity. Fine grinding and thorough mixing insures a uniform fusion product in the shortest possible time and hence minimum solution of opacifying agents and minimum reduction in opacity.

2. MELTING

In the smelter the enamel mixture is melted and fined until no lumps of unfused or undissolved material can be detected in a string of the glass drawn from the melt. The melting process begins with the fusion of the least refractory ingredients or fluxes—borax, soda ash, etc.—at relatively low temperatures. The liquid

attacks the more refractory substances both by solution and by chemical reaction. The formation of eutectics between the raw materials and the compounds resulting from chemical reaction facilitates the melting process.

If the smelting process is continued for a sufficient length of time a perfectly homogeneous glass in which all constituents would be in equilibrium would result. Such a condition is not obtainable, especially in white enamels. The melting should proceed only to the point where a stable borosilicate glass is formed, in which the opacifying agents, fluorides, tin oxide, and antimony compounds are carried in suspension. Longer smelting results in a considerable solution of these materials, as well as decomposition of the fluorides and consequent reduction in the opacity of the enamel. No opacity is obtained from tin or antimony oxides after they are once taken into solution. Quick smelting is therefore to be desired, and this again calls attention to the value of fine grinding and thorough mixture of the raw materials.

An interesting investigation of the effect of time of smelting on the nature of enamel frits has been made by Poste and Rice.¹⁴ As a result of the studies they have drawn the following conclusions:

1. Fluorine from fluorspar is all driven out of the enamel in the very early stages of smelting.

Strictly speaking, this applies especially to the particular enamel with which Mr. Poste is dealing, but it, no doubt, applies equally well to many other enamels. On the other hand, there is no doubt that in some enamels the fluorine will be retained after prolonged heat treatment.

2. The fusibility of the frit decreases as the time of fritting is increased.

3. Alkalies and boric acid decreases and silica increases as the time of fritting is increased.

This condition is brought about by volatilization of alkalies and boric acid. The curves obtained indicate that lime and alumina do not change. It would seem that these should vary the same as silica, in view of the fact that neither volatilizes to any extent.

4. The fusion range is greatest just at the point where the frit would normally be drawn from the smelter.

5. The ability of the frit to resist solutions increases as the length of time in the smelter is increased.

¹⁴ Poste, E. P., and Rice, B. A., *The Effect of the Degree of Smelting Upon the Properties of Enamel Frits*, Jour. Am. Ceram. Soc., 1, p. 221.



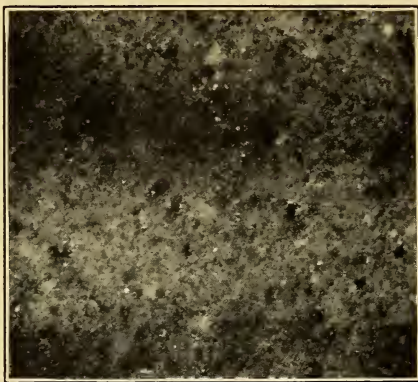


FIG. 1.—Sample A-1. *Underfired enamel, oblique illumination.* $\times 75$

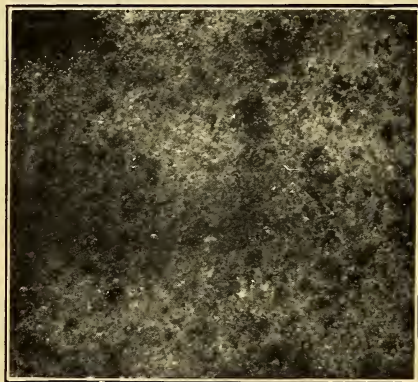


FIG. 2.—Sample A-2. *Properly fired enamel, oblique illumination.* $\times 75$

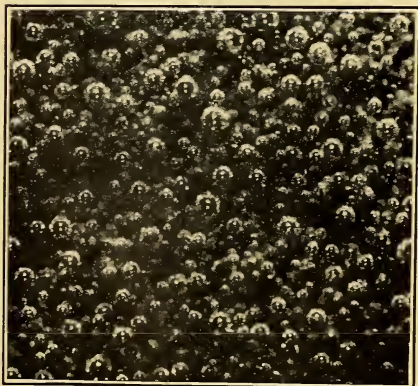


FIG. 3.—Sample A-3. *Overfired enamel, oblique illumination.* $\times 75$

The same investigators used a relatively soft formula, which is in commercial use, in making a series of trial cups which were burned under varying conditions. The first piece, designated as A-1, was underburned, but to a degree which would not carry it far beyond a commercial possibility. The second, A-2, was given as near the proper burn as possible, and the third, A-3, was somewhat overburned. The resulting pieces were examined under the microscope with oblique illumination and a magnification of about 75 diameters at the plate of the camera.

SAMPLE A-1.—A medium blue enamel with fair gloss, the surface being slightly rough to the touch. Under the microscope this enamel shows an indefinite field of unfused material and minute bubbles, with practically no large bubbles.

SAMPLE A-2.—The enamel is about the same in color as A-1, but has a much better gloss and is smooth to the touch. There is no surface pitting. The microphotograph shows a reasonably uniform field similar to that obtained from A-1, and in addition a noticeable distribution of large bubbles on a background containing unfused material and fine bubbles.

SAMPLE A-3.—The color of the enamel is much darker than A-1 and A-2. The gloss is very good, but there is a tendency for surface pitting. On magnification there is found to be a dark-blue background of homogeneous glass showing no unfused material. In the foreground is a very even distribution of large, well-formed bubbles.

3. TEMPERING ENAMEL SLIPS

In preparing enamel slips for application to the ware the frit is ground wet and contains 5 to 10 per cent (by weight) of plastic clay. To increase the viscosity of the slip and aid in holding the enamel in suspension, a flocculating agent is added. In white or cover enamels magnesium sulphate is generally used for this purpose. In ground coats borax is almost universally employed, since nearly all other salts which have a similar effect on the slip are likely to cause rusting of the steel during the drying of the ware.

Prior to the outbreak of the war the Vallender clay from Germany was almost exclusively used by enamellers in preparing their slips. This is a very clean and highly plastic clay. The necessity of finding a substitute for this material has brought on the market a number of American clays of varied quality. It was generally considered by enamellers that none of these satisfactorily replaced the German clay.

An investigation of the properties of several clays for enameling purposes was carried out by the writer¹⁵ with the object of finding a clay or a mixture of clays, American, if possible, which could be satisfactorily used to float enamels, preventing them from settling to the bottom of the dipping tub and permitting tempering to a proper consistency to obtain a uniform coating of desired thickness on the surface of the ware. It was thought that ball clays were most likely to give the desired result, but the Florida clay was included since it had been used for this purpose on different occasions. The clays selected were:

- No. 1. Kentucky ball clay.
- No. 2. Tennessee ball clay, J. K. Porter No. 11.
- No. 3. German Vallender clay.
- No. 4. Georgia clay.
- No. 5. Florida clay.
- No. 6. English ball clay, M. & M.
- No. 7. A clay supplied to the trade, resembling Florida clay, included in part of the tests.

A series of experiments was made, treating the clays with electrolytes, to determine their properties as compared with the Vallender clay. In all the clays the results showed some similarity to the German clay, but on the whole they may be placed in the order: Nos. 2, 5, 1 and 4, 6, as regards their resemblance to No. 3.

Experiments were next made to determine how the clays would act when used as the agent for floating the enamels.

There are five factors which greatly influence the floating of frits in enamel or glaze slips: (1) Size of grain of the frit; (2) specific gravity of the frit; (3) concentration of frit in the slip; (4) viscosity of the floating medium; (5) amount of the floating medium.

1. Fine grinding makes the frit more easy to float, but enamellers dare not grind too finely, because of difficulty in getting a uniform coating on the ware. Ground coat enamels especially must be coarse, not finer than 100 mesh, and, better, 80 mesh.

2. Lead enamels would, of course, be more difficult to float than lighter ones, but lead is seldom used in enamels for sheet iron. However, all frits are relatively high in specific gravity as compared with clays and therefore settle more readily.

3. Settling is easily prevented by making the slip thick, approaching a paste, but in order to apply them by dipping or spraying, slips must be sufficiently fluid to flow. With such a

¹⁵ Shaw, J. B., *American Clays for Floating Enamels*, Trans. Am. Ceram. Soc., 19; 1917.

consistency heavier substances will settle unless a floating agent is used.

4. Viscosity has been described as the friction between two liquids flowing in contact with each other, or between a liquid and a solid moving in it; in other words, resistance to flow. The efficiency of a floating medium in preventing the settling of heavier particles, therefore, depends upon its viscosity or resistance to the motion of particles passing through it. The floating medium in the case of enamels is not to be considered as the water, but as the clay substance in suspension in water.

High viscosity is also required in enamel slips to prevent them from flowing down the sides and into the corners of the ware after dipping. A steel body, being nonabsorbent, offers a different problem from that of a porous body dipped in a glaze slip. The absorption by the porous body prevents the flowing of the glaze, but the enamel slip must stay in place by virtue of its viscosity, although it is possible that surface tension also plays an important rôle here.

5. It is evident that a sufficient amount of the floating medium to prevent settling can readily be added, but other considerations limit the amount of clay which can be used with any glaze or enamel, about 10 per cent being the maximum permissible in the latter. The efficiency of the clay as a floating agent is therefore highly important, especially in enamels where the frit is of higher specific gravity and more coarsely ground than in glazes or engobes, and where the amount of clay used is necessarily small.

(a) **SETTLING OF THE ENAMEL.**—The relative amount of settling of the enamel when the several clays with different flocculating agents as the floating medium were used was determined as follows: The frit was ground dry to pass an 80-mesh screen, and the slip was prepared by weighing out frit and clay and adding the required amount of water and electrolyte. The slip was shaken for two hours.

In a second series of tests the slips were made up without other flocculating agents, ground wet to pass an 80-mesh sieve, and, after standing for 18 hours, were tempered with water and the electrolyte. They were then shaken by hand for 1 minute.

After shaking the slip, in both cases, it was allowed to stand for 18 hours. The volume of clear water on top was measured and this was decanted off. The weight and volume of the remaining slip was then determined and the upper half of this

decanted off. The weight and volume of the lower half of the slip was determined. From these measurements the amount of settling of the enamel was indicated by the amount of clear water over the slip after standing, and by the relative specific gravities of the original slip, of the residue after decanting off the clear water from the tubes after standing 18 hours, and of the lower half of this residue. The less the increase in specific gravity from that of the original slip to that of the lower portion in the tube after standing, the less the settling of the enamel.

The results showed the Tennessee ball clay (No. 2) to most nearly resemble the Vallender clay in ability to keep the enamel in suspension. The kaolins (Florida and Georgia) gave surprisingly good results in this respect.

It is to be noted that the conditions in this experiment do not conform exactly to those in the dipping tubs in enameling work where the stirring of the slip has the effect of washing out the heavier particles and facilitates sedimentation as soon as stirring ceases. Occasional stirring of the top part of the slip causes the frit to settle out and leaves the clay in suspension.

(b) VISCOSITY MEASUREMENTS.—In view of the importance of the degree of viscosity in enamel slips, considerable attention was given to the measurement of this in testing the floating properties of the clays. After trying several types of apparatus a viscosimeter was devised which gave excellent results in this work, and it is thought that a similar one might be used to advantage by enamelers in maintaining uniform consistency in their slips. It might also be of value in the preparation of glazes and engobes.

The apparatus¹⁶ consists of a brass cylinder, 1½ inches in diameter, provided at the bottom with two efflux tubes 1 inch long and of three thirty-seconds and five thirty-seconds inch bore, respectively. These are closed by caps, which are held in place by a spring. Graduated tubes are placed under each efflux tube to measure the amounts of slip which flow from these after releasing the spring holding the caps. The viscosity determination is based on the following considerations:

The quantity of liquid flowing through a short tube or orifice is represented by

$$Q = KA\sqrt{2gh}$$

where K is a constant for a given tube and liquid, its value depending upon the frictional resistance to flow, A is the area

¹⁶ Trans. Am. Ceram. Soc., 19, p. 349.

of the tube, and gh represents the velocity of flow. In this apparatus the flow through the two tubes, a and b , is represented by

$$Q_a = K_a A_a \sqrt{2 gh} \text{ and } Q_b = K_b A_b \sqrt{2 gh}.$$

The ratio of flow from the two tubes is

$$\frac{Q_a}{Q_b} = \frac{K_a}{K_b} \cdot \frac{A_a}{A_b} \cdot \frac{\sqrt{2 gh}}{\sqrt{2 gh}}.$$

Hence

$$\frac{K_a}{K_b} = \frac{Q_a}{Q_b} \cdot \frac{A_b}{A_a} = KX = \text{viscosity}.$$

In the case of water

$$Q_a = 45 \text{ cc, } Q_b = 15 \text{ cc,}$$

and

$$\frac{K_a}{K_b} = \frac{45}{15}, \frac{A_b}{A_a} = 3 \frac{A_b}{A_a}.$$

Since $\frac{A_b}{A_a}$ is constant, the values for relative viscosity with this apparatus may be expressed as $\frac{Q_a}{Q_b}$.

It is the general practice to refer viscosities to that of water as unity, but for comparative purposes it seems satisfactory to express the values as given by the instrument itself, whereby water gives a viscosity value of 3.

The viscosities of enamel slips made up with the different clays and with various electrolytes, and using different water contents, are shown in the curves of Figs. 4 to 6. The more rapid the increase in viscosity with increase in specific gravity of the slip, the better the action of the clay as a floating agent.

In Fig. 4 it is noted that the Tennessee ball clay is fully as good in this respect as the Vallender clay, while the Kentucky ball clay and a mixture of Tennessee and Florida clays are good, the latter being much the better.

In Fig. 5 the Vallender clay appears greatly superior to the others. The use of borax as the electrolyte conforms to general factory practice, and it is in enamels tempered with borax that the greatest difficulty in floating occurs.

A comparison of the curves in Figs. 4 and 5 shows that high viscosities are obtainable with slips of much lower weight per 100 cc when magnesium sulphate is used than when borax is used. A heavy slip is difficult to distribute uniformly on the ware and tends to flow down the vertical surfaces because of its high specific gravity, which tends to overcome the viscosity.

The enameler attempts to get the proper degree of viscosity with a slip of certain specific gravity and learns by practice to recognize the proper conditions. A viscosity value as low as 4.5 is permissible for enamel slips, if the weight per 100 cc does not much exceed 150 g. The low viscosities obtainable, when no flocculating agent is used, even with slips of high specific gravity, are shown in Fig. 6.

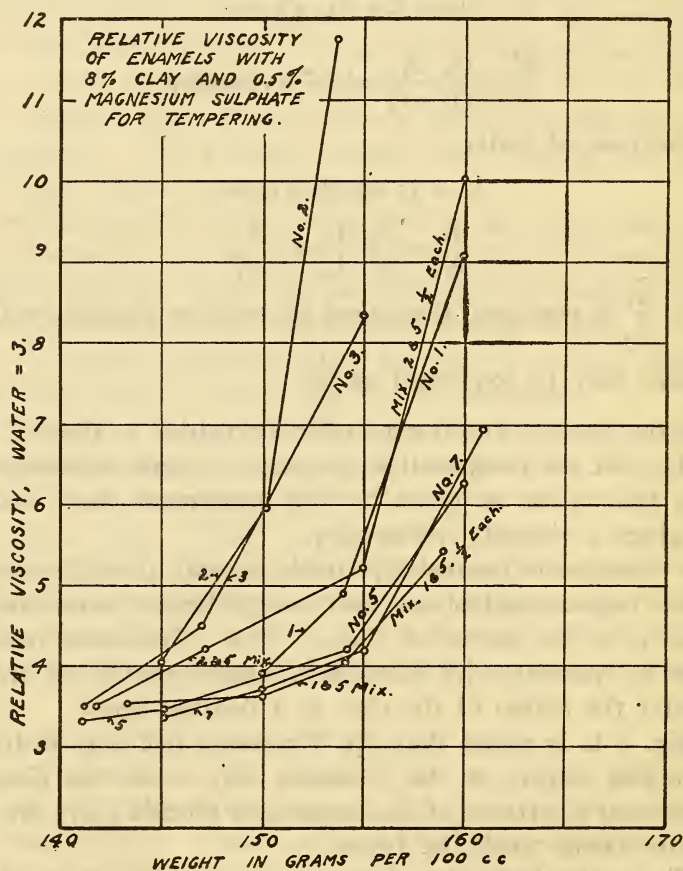


FIG. 4

Comparison of the results with the various slips and in the various tests shows little relative change in the position of the clays, but a decided difference in the effects of the various flocculating agents. The Vallender clay is apparently decidedly superior to the others; the Tennessee ball clay comes next, and is in some respects better than the Vallender. The Florida clay also shows good results.

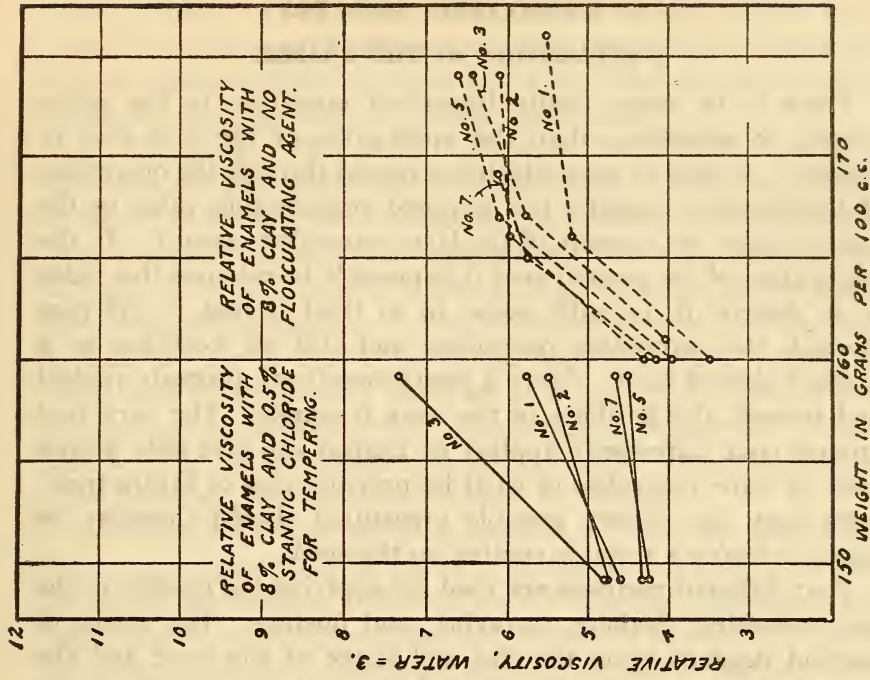


FIG. 5

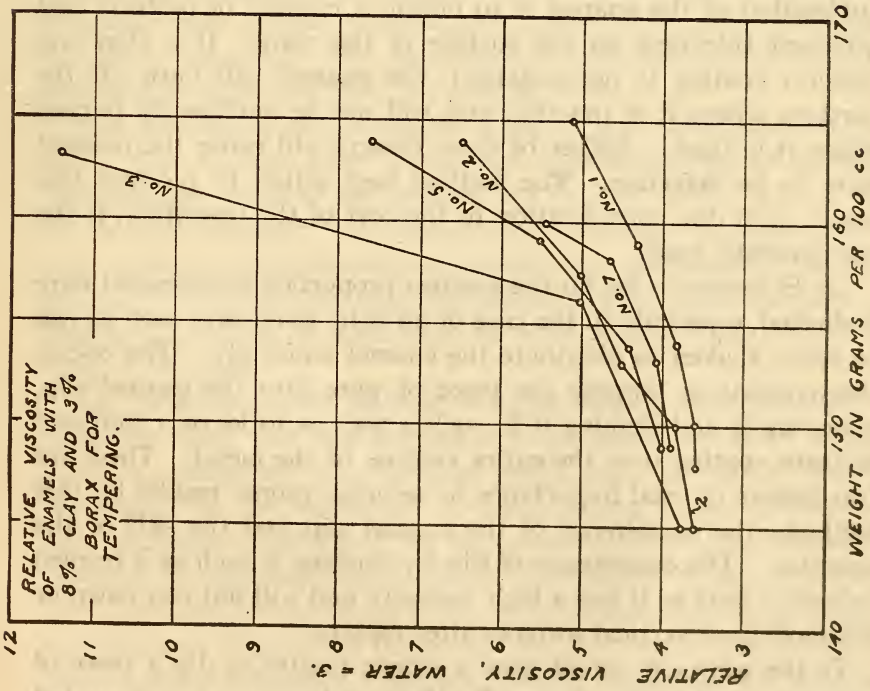


FIG. 6

V. ENAMELING PROCESS

1. APPLICATION OF THE ENAMEL

There is no more vitally important operation in the entire process of enameling than the application of the first coat of enamel. A piece of ware which has passed through the operations of forming and cleaning has acquired considerable value to the manufacturer on account of the labor expended upon it. In the application of the ground coat it is possible to enhance this value or to destroy it, or, still worse, to so treat it that it will pass through the succeeding operations and still be worthless as a finished piece of ware. Given a good ground coat, properly applied and burned, the finishing of the ware is simple. The very best ground coat improperly applied or burned can give only a poor piece of ware, regardless of what its previous cost or future treatment may be. Every possible precaution should therefore be taken to insure a suitable coating on the steel.

Four different methods are used for applying the enamel to the steel—slushing, draining, spraying, and dusting. The choice of method depends upon the size and shape of the ware and the nature of the enamel. The chief factor to be considered in the application of the enamel is to obtain a coating of uniform and sufficient thickness on the surface of the ware. If a thin and uniform coating is not obtained, the enamel will burn off the portions where it is too thin and will not be sufficiently burned where it is thick. Either of these defects will cause the finished ware to be defective. The method best suited to produce this result, with due consideration to the cost of the operation, is the one generally used.

(a) SLUSHING.—By far the greatest proportion of enameled ware is slushed, especially in the case of all light wares and such as can be easily shaken to distribute the enamel uniformly. The operation consists in dipping the piece of ware into the enamel slip, removing it and shaking it in such a way as to leave a thin and uniform coating over the entire surface of the metal. There are two factors of vital importance in securing proper results by this method—the consistency of the enamel slip and the skill of the operator. The consistency of slip for slushing is such as is termed “short;” that is, it has a high viscosity and will not run down or drain off from vertical surfaces after dipping.

To the novice it would seem a simple matter to dip a piece of steel into a tub of slip, shake off a little, and obtain a nicely coated

piece of ware. As a matter of fact, considerable practice is required to acquire skill sufficient to slush even simple shapes uniformly, while extensive training and a very high degree of skill is required in the handling of complicated shapes.

(b) DRAINING.—This method is frequently applied to perfectly flat ware, such as signs, and to simple shapes. The piece of ware is dipped in the slip and is then set on edge to allow the excess to run off at the bottom. The consistency of the slip, which is very different from that used in slushing, is the principal factor in the success of this operation. In this case the viscosity is much lower, so that the slip will flow down the vertical surface, but at the same time its consistency must be such that it will form a good coating and adhere to the ware after the excess drains off. It must also be sufficiently viscous to keep the enamel in suspension and not allow it to settle onto the bottom of the tank.

(c) SPRAYING.—For applying enamel to complex shapes and heavy ware, spraying is frequently resorted to. It is too expensive to use on the ordinary grades of ware, but for special shapes with many corners and sharp angles, or any piece of ware which can not be slushed uniformly, spraying is the best method of coating. It is wasteful of material and requires skill to obtain good results, but if proper care is used any piece of ware can be very uniformly coated by spraying. The piece may be placed on a whirling rack and turned while the spray is being applied.

The consistency of the enamel is highly important again in this case. The enamel must be ground sufficiently fine to prevent stopping the nozzle of the sprayer, but for best results it must not be too finely ground. Its viscosity must be high to prevent flowing. Since the distribution of the slip over the surface is accomplished in this case by the movement of the spray and not by shaking the piece, it is possible to work with a higher viscosity than in slushing.

(d) DUSTING.—This method of application is very common in cast-iron work, but in steelwork it is used only on heavy wares, such as condensers for chemical works, etc. It has a decided advantage in the production of acid-resisting wares, because no raw materials are added to the frit, whereas when any of the other methods of application are used, it is necessary to add some raw clay and soluble salts to the frit in order to get a slip of the proper consistency. These raw materials are invariably decidedly injurious to the enamel, especially where resistance to chemical

corrosion is desired. While an enamel is a glassy coating, it is far from being a solid glass; and the more raw material added in grinding the frit the further is the finished enamel removed from this condition, since these raw materials are only to a very slight extent combined with the frit during the brief burning operation. Because of this fact the dusting method is decidedly the best to use for making enameled ware to resist chemical corrosion.

In carrying out this process, the ground coat, as well as cover coat, is frequently dusted on. The metal is wiped with a wet sponge or cloth, and the powder dusted on while the metal is still wet. Sometimes an adhesive agent is added to prevent the enamel from falling off when dry.

The methods used for cover enamels are the same as those used for ground coats. The quality of workmanship in applying cover coats is far less important than in applying ground coats. If a piece of ware is perfectly coated with the ground coat, the cover coat may be quite imperfectly applied and still give good results. Of course there are limits to this, and the more uniformly the enamel is applied the better it will be. It should be said, further, that best results are always obtained with thin enamels. Barring the properties of whiteness and opacity, the excellence of enamels is inversely proportional to their thickness. This is especially true of the ability of the ware to withstand bending and abrasion. In view of these facts the aim should always be to keep the enamel as thin as possible, while at the same time obtaining the desired opacity and color.

2. DRYING

Ground-coat enamels should be dried as rapidly as possible to prevent rusting of the steel. This will be controlled to some extent by the flocculating agents used in the slip, but rapid drying is the best practice in any case. If an alkaline flocculating agent is used for tempering the ground coat, it can be dried in the open air without serious rusting; but if chlorides or sulphates are used, rusting is almost sure to result even with rapid drying. This rust may or may not be visible after the ware is dry, but it is quite sure to make its appearance, when the ground coat is burned, in the form of spots where the iron oxide has reacted with the enamel to such an extent as to form a spot-like iron scale. When these spots are formed, it is practically impossible to cover them with cover enamel. They will show in the finished ware either as dark spots or as pits in the surface. While proper drying of the ground coat can not entirely prevent this trouble in an improperly tempered

enamel, it will always reduce the trouble, and when the ware is not dried rapidly the trouble is likely to come even in the best tempered enamel.

The rate of drying of cover enamels is of less importance than in drying ground coats. However, rapid drying is here again desirable. One of the chief reasons for this, especially in white enamel, is the fact that dirt in the form of factory dust sticks to the ware while wet, and therefore rapid drying of the white enamel makes for pure white ware. Another point in favor of rapid drying of finished ware is the need of space for storing the ware. After the enamel is dry the ware can be handled and stored in much less space than when wet, and in making some classes of wares, such as cooking utensils, the problem of finding room for storing sufficient ware to keep the furnaces going is sometimes troublesome. There are two common defects caused by improper drying. Water streaking, caused by moisture from drying ware condensing on the cold surface of wet ware and running down vertical surfaces in streaks, can be avoided by proper circulation of air in the dryer. When ware is dried too rapidly the enamel will crawl. This is caused by the formation of shrinkage cracks due to driving off the moisture from the clay too rapidly. These cracks do not show in the dry ware, but when it is burned the enamel crawls and collects in beads. This defect will be caused when a piece of wet ware is set on a hot piece of metal or when the drying is very sudden. The same defect may result from rough handling of the dry ware, a sudden sharp blow breaking the bond between the dry enamel and steel, which results in crawling.

3. BURNING ENAMELS

(a) GENERAL DESCRIPTION.—Muffle furnaces are almost invariably used for burning light wares and especially white ware. For burning heavy steel wares open furnaces are used.

The general practice is to have a burner and a helper working on a furnace. The helper will acquire skill as a burner after he has worked on the furnace a few months under the tutoring of the experienced burner. The importance of this period of apprenticeship is generally overestimated. One of the best burners the writer has ever known was given charge of the burning on a furnace after spending only two days as helper. He spoiled some ware during his first few hours of burning, but in a few days he could be trusted to burn any ware as safely as old burners who had years of experience. Several cases similar to this have been observed, all pointing to the fact that if a man has ordinary intelligence he

can learn to burn enameled ware satisfactorily with very little experience.

The ware is set on pointed projections from iron grates, which should be kept sharp so that the least possible part of the grates comes in contact with the enamel. Only pieces of approximately the same size and weight should be burned together, since only a few minutes are allowed for burning a fork of light steel ware, and if there is much difference in the size of the ware it will heat up to the temperature of the furnace at different rates. As a result of this the lighter ware will be sufficiently fired before larger pieces have acquired the desired temperature, and some of the ware will be sure to be imperfectly fired.

In setting the ware on the grates preparatory to firing, care should be taken to see that ample space is left between all surfaces. Heavy parts like handles on dishpans and ears on kettles should be removed as far as possible from all other surfaces. The reason for this is not only to permit these heavy parts to heat up as rapidly as possible but also to prevent them from absorbing radiated heat from parts near them, thereby retarding the rate at which these parts are heated.

It frequently happens that there will be a small area on a piece of ware underburned while the piece as a whole is properly burned. Investigation of the cause of this will reveal the fact that this underburned spot was in close proximity to some heavy piece of metal or other surface which absorbed the heat while the main body of the piece of ware was free to heat up rapidly. A good burner will strike the happy medium and leave his ware in the furnace long enough to fire the heavy parts properly but not long enough to burn off the light parts. The nature of the enamel influences very materially the burner's ability to properly burn light and heavy parts, but he can greatly facilitate matters by using proper care in setting his ware on the grates.

The temperatures used for burning enamels differ widely, depending upon the enamel and the ware. General practice is to burn the ground coat at much higher temperature than the finishing coats. This is not due to the fact that the ground coat necessarily has a higher softening temperature than the finishing coats, but rather to the fact that it has been found that the general excellence of the ware is improved by this procedure.

(b) TEMPERATURE OF BURNING.—In order to determine the effect of burning at different temperatures, the following series of experiments was performed:

Trial pieces were made of No. 20-gage, United States Standard, open-hearth steel, cut into strips. These were carefully pickled with hydrochloric acid and coated with an enamel which was at that time in commercial use in a factory. The ground coat was applied on both sides of the test pieces by slushing, and two white coats were applied in the same manner on one side. To insure uniformity in application of the enamel, one man dipped all the trials. The ground and white coats used were of the following compositions:

GROUND-COAT FRIT		WHITE-COAT FRIT	
Borax.....	90	Borax.....	100
Soda ash.....	23	Soda ash.....	54
Potash feldspar.....	110	Potash feldspar.....	110
Quartz.....	70	Flint.....	110
Manganese dioxide.....	18	Saltpeter.....	23
Saltpeter.....	18	Fluorspar.....	13
Cobalt oxide.....	1.5	Barium carbonate.....	25
Fluorspar.....	27	Antimony oxide.....	20
		Zinc oxide.....	25
		Cryolite.....	25
MILL ADDITION		MILL ADDITION	
Clay.....	per cent.. 8	Tin oxide.....	per cent.. 6
Water.....	do.... 50	Clay.....	do.... 6
Magnesia.....	do.... .25	Magnesium sulphate.....	do.... .5
Borax in boiling solution.....	do.... 2.0		

Three different burning temperatures were used for each of the three enamel coats, the furnace temperatures being measured by means of a platinum platinum-rhodium thermocouple. The burning of the trial pieces was intrusted to the best burner in the plant with instructions to obtain the best results on each coat at the given temperatures. The trial pieces were numbered in accordance with the burning temperatures of the three coats. The first digit of the number indicates the temperature used for the ground coat; the second and third digits show the temperatures for the first and second white coats, respectively. The key to the burning temperatures used, with their index numbers and the time required in each case to produce the best results in the enamel, are as follows:

Ground coat			First white			Second white		
Index No.	Temperature	Time	Index No.	Temperature	Time	Index No.	Temperature	Time
	°F	Min-utes		°F	Min-utes		°F	Min-utes
1.....	1700	4	1.....	1600	2	1.....	1500	3
2.....	1800	3	2.....	1700	1½	2.....	1600	2
3.....	1900	2	3.....	1800	1	3.....	1700	1½

The numbering system for the trial pieces shows exactly the burning treatment in each case, as given above and below. The number "111" therefore indicates, by the initial index No. 1, that the ground coat was burned at 1700° F (see table above), and by the second index No. 1, that the first white coat was burned at 1600° F, and the third "1" shows that the second white coat was burned at 1500° F. Likewise trial No. 223 shows automatically that the burning was as follows: "2," ground coat, 1800° F; "2," first white, 1700° F; "3," second white, 1700° F.

BURNING TREATMENTS OF TRIAL PIECES

(For key to numbering system see above)

111	211	311
112	212	312
113	213	313
121	221	321
122	222	322
123	223	323
131	231	331
132	232	332
133	233	333

The burned trials were examined for surface defects and compared as to gloss and general excellence of quality. Tests were made to determine their ability to withstand abrasion and bending and sudden change of temperature. In the last test several trials were made before comparative results could be obtained. The pieces were heated first to a dull red and plunged into cold water. The trial pieces withstanding this treatment were Nos. 313, 321, 322, 323, 331, 332, 333, 231, and 131. Nos. 311 and 312 were only slightly chipped.

In the bending test the trial pieces were bent around a 1¼-inch pipe with the white-coated surface on the inside. The following trials withstood this test without indication, to the unaided eye, of rupture: Nos. 111, 121, 231, 331, and 332, showing excellent toughness and flexibility of the enamel. All the trials withstood bending to a right angle before the enamel came off.

In examining the pieces for surface defects, gloss, and general excellence of quality, it was noted that the best appearance was always obtained with the lowest temperature of burning of the final coat, regardless of the treatment for the preceding coats. Black specks and dull enamels resulted from high temperatures of burning the finish coat.

The following conclusions were drawn from the results of the tests:

1. The test pieces on which the ground coat was burned at the highest temperature were best able to withstand sudden change of temperature.
2. The ability of the enamel to withstand abrasion, bending, or sudden change of temperature is greatest when the temperature at which the finishing coat is burned is decidedly lower than that at which one of the preceding coats has been burned.
3. A low temperature can be used for burning the ground coat, provided it is burned "done," and a high temperature is used for burning first coat white.
4. To prevent pinholes and black specks a high heat should be used for either ground coat or first coat white, and a much lower heat for finish white.

For best results with this enamel, the ground coat should not be burned below 1700° F, and the first coat white should be nearly as high. The finish white should be burned at a temperature at least 100° below either the ground coat or the first coat white. Temperatures recommended for these enamels are about as follows: Ground coat, 1800° F; first white coat, 1750 to 1800° F; finish white, 1600 to 1650° F.

While the results obtained here can be strictly applied to these enamels only, experience in using many other enamels confirms the conclusions reached in this series of experiments.

Obviously no fixed rule can be laid down for burning enamel wares, since different shapes and sizes can be best burned under different conditions. The production of some enamels requires high temperatures for burning, and, unfortunately, these enamels are sometimes applied to very large pieces, which have a great tendency to warp during burning. Furthermore, it is commonly the case that several pieces must be joined after enameling, this fact making it essential that the warpage be reduced to a minimum. Since the tendency to warp increases with increase of temperature, it will be readily seen that the production of this class of ware requires the striking of a medium as regards time and temperature of burning which will give an enamel of the desired quality while at the same time causing little warpage of the ware.

In making cooking utensils and some other shapes of light-gage steel, the wire is straightened while still hot after coming from the furnace. Warpage will be greatly reduced by using proper

care in supporting the ware during burning. Every precaution should be taken to see that the ware is supported at a sufficient number of points and at proper points to prevent warping.

Just as emphasis was laid on the proper slushing of first coats of enamels, so also must the importance of proper burning of the first coat be emphasized. Improper burning of the first coat produces a large amount of defective ware. It is essential that the first coat be properly and uniformly applied in order to be properly burned, but proper burning is absolutely necessary if a good piece of ware is to result. This is left to the judgment of the burner, who estimates from the appearance of the specimen when it has been properly burned. Proper burning can be accomplished at different temperatures by suitable adjustment of the time.

The first coat, when properly burned, seldom has a high luster, but will not be dead. A blue or purple color indicates underburning, which will result in "fish scale" or jumping off upon application of the cover coat. A dead-black or a green color indicates overburning, which will be difficult to cover with white and may result in jumping off or in fish scale of a type different from that of underburning. Fish scale on underburned ware generally results in flakes from one-sixteenth to one-eighth inch in diameter jumping off, while fish scale from overburning results in very minute flakes popping off in great numbers. Running the hand over a piece of overburned ware produces a snapping sound. Sometimes the fish scaling will not start until the first coat of white is run into the furnace, or fish scaling may not develop at all, but the enamel will not adhere properly and the ware is sure to be short-lived.

VI. CALCULATION OF ENAMEL FORMULAS

1. METHODS EMPLOYED

Several methods of expressing quantitatively the compositions of glasses, glazes, and enamels have been devised. In most of these it is the purpose to indicate the relative proportions of the components remaining after the melting process, in which volatile matter is expelled from the raw ingredients. Among the methods of expressing compositions are:

1. COMPOSITION IN PERCENTAGES OF RAW MATERIALS USED.—This corresponds to the batch weights and does not attempt to show the composition of the finished product. An advantage is claimed for this method in that it recognizes differences in effect

of various raw materials which may be so combined as to produce the same final product, so far as chemical analysis would show in various mixtures, but in which these different materials produce different melting behaviors and possibly different physical properties.

2. COMPOSITION IN PERCENTAGES OF THE OXIDES IN THE PRODUCT.—This corresponds to the result obtained by chemical analysis.

3. COMPOSITION IN TERMS OF EUTECTICS.—Some use of combinations of eutectic mixtures of various oxides or minerals has been made to produce fusible compositions for glazes.¹⁷ Owing to the lack of information on the eutectics formed between components used in enamel mixtures, this method is not at present practical for expressing enamel formulas.

4. COMPOSITION IN TERMS OF NORMS.¹⁸—This attempts to express the formula in terms of minerals considered as most likely to be formed in the fusion of the raw materials used in the mixture. It has been proposed for use in compounding glazes but has not been applied to enamels.

5. EMPIRICAL FORMULA.—This attempts to represent the composition of the fusion product of a mixture in molecular proportions of the oxides present. Regarding this method, objection is made that it attempts but does not realize the representations of the chemical constitution, and that it is unscientific and cumbersome. It may be noted in this connection that many of our chemical formulas do not express actual compositions but only relative proportions of elements. Their value is not, however, lost by this fact. The empirical glaze, or enamel formula, is merely a means of expression and a tool which has proved valuable as an aid to study and comparison of various combinations of materials.

2. COMPOSITION IN TERMS OF OXIDES

The fritted weight of an enamel may be closely approximated by calculating the quantity of oxide capable of being formed by the elements incorporated into the batch. Several factors enter into fritting which make it impossible to figure the exact weight of frit obtainable from a given quantity of raw material of which the exact composition is known. Among these may be mentioned

¹⁷ Watts, A. S., A Study of Bristol Glazes Compounded on the Eutectic Basis, *Trans. Am. Ceram. Soc.*, **18**, 1916; The Practical Application of Bristol Glazes Compounded on the Eutectic Basis, *Trans. Am. Ceram. Soc.*, **19**, 1917.

¹⁸ Staley, H. F., The Calculation of Ceramic Mixtures, *Trans. Am. Ceram. Soc.*, **13**, 1911.

loss during charging the smelter by chemicals being carried away by the draft, volatilization of some of the metallic elements, and lack of complete decomposition of some of the raw materials, notably fluorides. However, in spite of these discrepancies, the calculated fritted weight will generally approximate quite closely the actual weight obtained.

In enamel calculations it is assumed that the following materials are not volatile: silica, flint, sand, SiO_2 ; zinc oxide, ZnO ; litharge, PbO ; tin oxide, SnO_2 . Antimony is more or less volatile, according to the conditions and intensity of heat treatment during melting. In calculating formulas the usual practice is to assume that 100 per cent is retained.

The accompanying table (Table 2), based upon chemically pure materials, shows the fritted weight of the oxides obtained when the other raw materials ordinarily used in enamels are completely decomposed under the influence of heat in an oxidizing atmosphere.

TABLE 2.—Fritted Weights as Per Cent of Weight of Pure Raw Material

Material	Potas- sium oxide (K_2O)	Sodium oxide (Na_2O)	Calci- um oxide (CaO)	Magne- sium oxide (MgO)	Lead oxide (PbO)	Barium oxide (BaO)	Alumi- num oxide (Al_2O_3)	Silicon di- oxide (SiO_2)	Boric oxide (B_2O_3)
Feldspar.....	17						18	65	
Red lead.....					97				
White lead.....					86				
Barium carbonate.....						78			
Calcium carbonate.....			56						
Fluorspar ^a			72						
Cryolite ^a		44					24		
Soda ash.....		58							
Sodium nitrate.....		36							
Saltpeter or potassium nitrate.....	47								
Magnesium carbonate.....				48					
Borax.....		16.2							36.6
Boracic acid.....									56.4
Clay.....							39	47	

^a The fusion product obtained from fluorides is variable and uncertain. The values given are based on the assumption that the fluorides are completely decomposed.

The following illustrates the use of the table in finding the fritted weight of an enamel:

	Pounds raw	Per cent of oxides	Pounds frit	Pounds lost
Feldspar	100	{ 17.0 18.0 65.0	17.0 K ₂ O	
Flint	100	100.0	18.0 Al ₂ O ₃	
			65.0 SiO ₂	
Borax	100	{ 16.2 36.6 47.2	100.0 SiO ₂	
			16.2 Na ₂ O	
Soda ash	50	{ 36.6 47.2 58.0	36.6 B ₂ O ₃	47.2 H ₂ O
			29.0 Na ₂ O	
Salt peter	10	{ 42.0 47.0 45.0		21.0 CO ₂
			4.7 K ₂ O	
Fluorspar	30	{ 8.0 72.0 19.0		4.5 NO ₂
			21.6 CaO8 O ₂
Cryolite	50	{ 44.0 24.0 54.0	22.0 Na ₂ O	14.7 F
			12.0 Al ₂ O ₃	
Antimony oxide	40	100.0		22.0 F
Tin oxide	20	100.0	40.0 Sb ₂ O ₃	
Zinc oxide	15	100.0	20.0 SnO ₂	
			15.0 ZnO	
Total	525		417.1	110.2

The calculation of the fritted weight of an enamel can be simplified by use of the curves in Fig. 7. Each curve shows the weight of one oxide per 100 pounds of the raw material introduced, or the percentage of the original weight.

Illustration: To find the fritted weight of a white enamel of the following composition:

Feldspar	178.0	Fluorspar	10.5
Flint	140.0	Cryolite	59.5
Borax	83.0	Tin oxide	34.0
Soda ash	15.0		
Salt peter	16.0		
			536.0

Feldspar is found represented on three curves, 2, x , and 15, showing the weight of potassium oxide, alumina, and silica, respectively, resulting from the fritting of 100 pounds of feldspar.

To determine the weight of potassium oxide resulting from the 178 pounds of feldspar used, follow the horizontal line corresponding to 178 pounds raw material to the right until it intersects curve No. 2; then drop vertically and read the pounds of oxide on the base line, in this case 30. Following the same procedure it is found that the horizontal line corresponding to 178 pounds of raw

material intersects curves x and 15 on vertical lines corresponding to 32 and 115.5 pounds of alumina and silica, respectively. The same method is followed for the other raw materials. In some cases the intersection of the curves falls near the lower left-hand corner of the sheet, where the exact location of the point is difficult

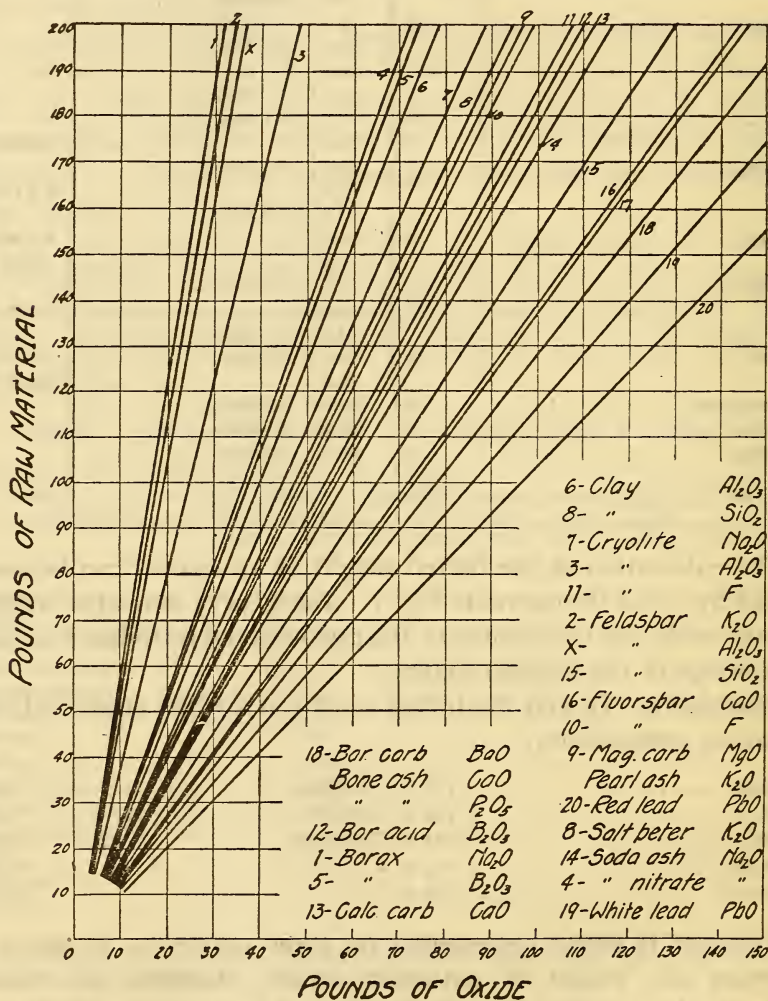


FIG. 7.—Chart for obtaining pounds of oxide from pounds of raw material

to determine. In such a case a multiplier may be used for the raw material and the same number will then be used as a divisor for the resulting weight of the oxide. Thus, in the case of soda ash, the intersection of the horizontal line for 15 pounds of raw material with curve 14 is not easily determined, but the weight of soda ash may be multiplied by 10. The weight of sodium oxide resulting

from 150 pounds of the ash is 87 pounds. Then, dividing this by 10, the amount of sodium oxide derived from 15 pounds of the ash is 8.7 pounds. Other multipliers may be used when convenient.

Following the same procedure for all the raw materials in the batch, the results obtained may be tabulated as follows. The fritted weight is obtained by adding the weights of the oxides. The composition may be expressed in percentage of the oxides by dividing the weight of each by the fritted weight of the enamel:

Batch	Potassium oxide (K ₂ O)	Sodium oxide (Na ₂ O)	Calcium oxide (CaO)	Alum- ina (Al ₂ O ₃)	Boric oxide (B ₂ O ₃)	Silica (SiO ₂)	Tin oxide (SnO ₂)	Fluor- ine (F)
178 feldspar.....	30.0	32.0	115.5
140 flint.....	140.0
83 borax.....	13.0	31.0
15 soda ash.....	8.7
16 saltpeter.....	7.5
10.5 fluorspar.....	7.5	5.2
59.5 cryolite.....	26.0	14.0	32.0
34 tin oxide.....	34.0
Fritted weight.....	37.5	47.7	7.5	46.0	31.0	255.5	34.0	37.2
Percentage composition....	7.56	9.60	1.51	9.27	6.25	51.46	6.85	7.50

These curves are based on chemically pure materials, but similar curves may be drawn for any substance of known composition. Allowance may also be made for the moisture content of a material in the preparation of such curves.

3. MOISTURE FACTOR

It is frequently the case that raw materials for enamels contain considerable percentages of moisture. In order to maintain correct compositions it is necessary to make allowance for the moisture content in making up the batch. The moisture content is easily determined by weighing a sample of a material, carefully drying it, then weighing the dried material. The percentage loss is generally based on the weight of dry material. The moisture factor represents the weight of raw material necessary to give 1 pound of dry material or $\left(1 + \frac{x}{100}\right)$ where x = per cent moisture content in terms of dry weight.

For example, a sample of flint from the bin weighs 10 pounds before and 9 pounds after drying, the moisture loss being 1 pound. The moisture content in percentage of dry weight is $\frac{1}{9} \times 100 = 11.1$ per cent. In order to obtain a definite weight of dry flint, the

weight of material taken from the bin must be $\frac{10}{9} = 1 + \frac{11.1}{100} = 1.11$ times the dry weight required. This figure 1.11 represents the moisture factor in this case. If the moisture were not taken into account in preparing an enamel batch with such flint, there would be a very appreciable error in the composition of the enamel. Such a moisture factor in powdered flint or quartz is uncommon, but the importance of determining the moisture content of raw materials is obvious

4. EMPIRICAL FORMULA

The empirical formula, or the ceramic formula, as it is sometimes called, has been found to be a convenient means of representing the compositions of ceramic materials, minerals, etc., as well as those of glazes and enamels. The computation of the empirical formula is not a difficult matter and requires only a limited knowledge of chemistry, principally the symbols and atomic weights of the elements.

All chemical compounds are made up of elementary substances or elements, which are distinct kinds of matter. The compounds are formed by combination of the elements in definite proportions. As a matter of convenience the kinds and amounts of the elements forming a compound are represented by symbols and numerical factors. Each element is represented by a letter symbol, as Al for aluminum and O for oxygen. These symbols indicate that certain definite relative weights of the elements for which they stand are present in the compound. Thus the symbol Al represents 27 parts by weight of aluminum. This weight is known as the atomic weight. When more than one atomic weight of an element is present in a compound, this is indicated by numerical subscripts. Thus, alumina, which is made up of 2 atoms, by weight, of aluminum and 3 of oxygen, is written Al_2O_3 , the subscripts following the symbol of each element showing the number of atoms of that substance in the compound. Silica is represented by SiO_2 , water by H_2O , etc.

From the relative weights of the elements—atomic weights—and the number of atoms of each in the compound, the relative weight of the compound—molecular weight—may be calculated. Thus the molecular weight of Al_2O_3 is $(2 \times 27) + (3 \times 16) = 102$; of SiO_2 , $28 + (2 \times 16) = 60$, etc. The term "formula weight" may be used instead of molecular weight for ceramic calculations. The formula weight of a compound or molecule is simply the weight indicated by the formula. Often several compounds or

molecules are united to form a more complex compound or molecule.

The accompanying table gives the names, symbols, and atomic weights in round numbers of the elements commonly found in enamels. For a more complete list textbooks on chemistry should be consulted.

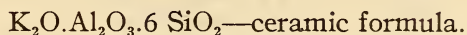
TABLE 3.—Atomic Weights of Elements Commonly Found in Enamels

Element	Symbol	Atomic weight	Element	Symbol	Atomic weight
Aluminum.....	Al	27	Magnesium.....	Mg	24
Antimony.....	Sb	120	Manganese.....	Mn	55
Barium.....	Ba	137	Nickel.....	Ni	59
Boron.....	B	11	Nitrogen.....	N	14
Calcium.....	Ca	40	Oxygen.....	O	16
Carbon.....	C	12	Phosphorus.....	P	31
Chromium.....	Cr	52	Potassium.....	K	39
Cobalt.....	Co	59	Silicon.....	Si	28
Copper.....	Cu	64	Sodium.....	Na	23
Fluorine.....	F	19	Sulphur.....	S	32
Hydrogen.....	H	1	Tin.....	Sn	119
Iron.....	Fe	56	Zinc.....	Zn	65
Lead.....	Pb	207			

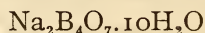
The empirical formula expresses the composition in molecular proportions of the various oxides which would be obtained by chemical analysis rather than in terms of the ratio of atoms of the elements present. Thus, the chemical formula of orthoclase or microcline may be written as



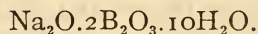
or



The latter is much more conveniently used in ceramic calculations. It represents the composition as being in the ratio of 1 molecule of potassium oxide to 1 of alumina to 6 of silica. Similarly the formula of borax may be written in the two ways as



or



The empirical, or ceramic, formula of a material is calculated from the chemical analysis in the following manner: The percentage, by weight, of each oxide is divided by its molecular weight, giving the relative molecular proportion of each in the material. In order to obtain a definite basis for comparison and use of such compositions, some portion of the formula is expressed

as unity, generally the sum of the basic oxides. Using the sum of the molecular proportions of the basic oxides as a divisor, the value obtained for each oxide is divided by this amount to obtain the ratio of molecular parts in terms of basic oxides as 1. An example of the method is as follows:

CHEMICAL ANALYSIS OF FELDSPAR

Potassium oxide, K_2O = 16.9 per cent by weight;

Aluminum oxide, Al_2O_3 = 18.4 per cent by weight;

Silicon dioxide, SiO_2 = 64.7 per cent by weight.

Dividing the percentage of each oxide by its molecular weight gives

K_2O $16.9 \div 94 = 0.18$ molecular parts;

Al_2O_3 $18.4 \div 102 = .18$ molecular parts;

SiO_2 $64.7 \div 60 = 1.08$ molecular parts.

To express the molecular ratio of oxides in terms of basic oxides as unity, divide the above values by that of K_2O :

$$\frac{0.18}{0.18} = 1 \text{ } K_2O \quad \frac{0.18}{0.18} = 1 \text{ } Al_2O_3 \text{ and } \frac{1.08}{18} = 6 \text{ } SiO_2.$$

The empirical formula is $K_2O \text{ } Al_2O_3 \text{ } 6SiO_2$.

The empirical formula of any material, including that of an enamel, may be calculated from its percentage composition in the same manner.

5. CALCULATION OF EMPIRICAL FORMULA FROM CHEMICAL ANALYSIS

The analysis of an enamel is as follows:

K_2O	6.5	Al_2O_3	4.7
Na_2O	17.5	SiO_2	43.3
BaO	5.5	B_2O_3	10.0
ZnO	6.0	SnO_2	7.5
CaO	5.6		

The relative molecular proportions of the oxides is determined by dividing the percentage of each by its molecular weight:

$$6.5 \div 94. = 0.069 \text{ } K_2O;$$

$$17.5 \div 62. = 0.280 \text{ } Na_2O;$$

$$5.5 \div 153. = 0.036 \text{ } BaO;$$

$$6.0 \div 81. = 0.074 \text{ } ZnO;$$

$$5.6 \div 56. = 0.100 \text{ } CaO;$$

$$4.7 \div 102. = 0.046 \text{ } Al_2O_3;$$

$$43.3 \div 60. = 0.721 \text{ } SiO_2;$$

$$10. \div 70. = 0.143 \text{ } B_2O_3;$$

$$7.5 \div 151. = 0.050 \text{ } SnO_2.$$

MOLECULAR RATIO OF OXIDES

$$\left. \begin{array}{l} 0.069 \text{ K}_2\text{O} \\ .280 \text{ Na}_2\text{O} \\ .036 \text{ BaO} \\ .074 \text{ ZnO} \\ .100 \text{ CaO} \end{array} \right\} 0.046 \text{ Al}_2\text{O}_3 \left\{ \begin{array}{l} 0.721 \text{ SiO}_2 \\ .143 \text{ B}_2\text{O}_3 \\ .050 \text{ SnO}_2 \end{array} \right.$$

.559—sum of basic oxides.

Dividing through by 0.559 to obtain the ratio on the basis of unit basic oxides (RO), the empirical formula is obtained:

$$\left. \begin{array}{l} 0.123 \text{ K}_2\text{O} \\ .502 \text{ Na}_2\text{O} \\ .064 \text{ BaO} \\ .132 \text{ ZnO} \\ .179 \text{ CaO} \end{array} \right\} 0.082 \text{ Al}_2\text{O}_3 \left\{ \begin{array}{l} 1.28 \text{ SiO}_2 \\ .25 \text{ B}_2\text{O}_3 \\ .09 \text{ SnO}_2 \end{array} \right.$$

1.000

The accompanying table (Table 4) gives the name, ceramic formula, molecular weight, and melted weight of pure raw materials ordinarily used in enamels.

TABLE 4.—Description of Pure Enameling Raw Materials

Name	Ceramic formula	Formula weight	Fusion product	Melted weight
Alumina.....	Al ₂ O ₃	102	Al ₂ O ₃	102
Antimony oxide.....	Sb ₂ O ₃ ^a	287	Sb ₂ O ₃ ^a	287
Barium carbonate.....	BaCO ₃	197	BaO.....	153
Boric acid.....	B ₂ O ₃ 3H ₂ O.....	120	B ₂ O ₃	70
Boric oxide.....	B ₂ O ₃	70	B ₂ O ₃	70
Calcium carbonate.....	CaCO ₃	100	CaO.....	56
Carbonate of lime.....				
Calcium fluoride.....	CaF ₂	78	CaO.....	56
Fluorspar.....				
Quicklime.....	CaO.....	56	CaO.....	56
Calcium phosphate.....				
Bone ash.....	3 CaO P ₂ O ₅	310	3CaO.....	3×56=168
Chromium oxide.....	Cr ₂ O ₃	153	Cr ₂ O ₃	153
Cobalt oxide.....	Co ₃ O ₄	123	Co ₃ O ₄	123
Copper oxide.....	CuO.....	80	CuO.....	80
Iron oxide (red).....	Fe ₂ O ₃	160	Fe ₂ O ₃	160
White lead.....				
Basic lead carbonate.....	Pb(OH) ₂ 2PbCO ₃	775	3PbO.....	3×223=669
Lead oxide (yellow).....				
Litharge.....	PbO.....	223	PbO.....	223
Lead oxide (red).....				
Minium.....	Pb ₃ O ₄	685	3PbO.....	3×223=669
Carbonate of magnesia.....	MgCO ₃	84	MgO.....	40
Magnesia.....	MgO.....	40	MgO.....	40
Manganese dioxide.....	MnO ₂	87	MnO ₂	87
Black oxide of nickel.....	Ni ₂ O ₃	165	Ni ₂ O ₃	165

^a It is customary to consider commercial oxides as being Sb₂O₃. In reality, they are mainly Sb₂O₄, formula weight 488. Probably during fusion antimony oxide is converted to the pentoxide, Sb₂O₅, in which case the melted weight is 351.

TABLE 4—Continued

Name	Ceramic formula	Formula weight	Fusion product	Melted weight
Potassium carbonate.....	K_2CO_3	138	K_2O	94
Pearl Ash.....	KNO_3	101	K_2O	94
Potassium nitrate (saltpeter).....	$K_2O \ N_2O_5$	202	K_2O	94
Sodium borate.....	$Na_2O \ 2B_2O_3 \ 10H_2O$	382	$Na_2O \ 2B_2O_3$	202
Borax.....	Na_2CO_3	106	Na_2O	62
Soda ash.....	$Na_2CO_3 \ 10H_2O$	286	Na_2O	62
Sodium carbonate crystals.....	$NaNO_3$	85	Na_2O	62
Sodium nitrate (Chili saltpeter).....	$Na_2O \ N_2O_5$	170		62
Silica:				
Flint.....	SiO_2	60	SiO_2	60
Quartz.....				
Sand.....				
Silicon fluoride.....	SiF_4	104	SiO_2	60
Tin oxide (white).....	SnO_2	151	SnO_2	151
Zinc oxide.....	ZnO	81	ZnO	81
Feldspar (orthoclase).....	$K_2O \ Al_2O_3 \ 6SiO_2$	556	$K_2O \ Al_2O_3 \ 6SiO_2$	556
Clay (kaolinite).....	$Al_2O_3 \ 2SiO_2 \ 2H_2O$	258	$Al_2O_3 \ 2SiO_2$	222
Cryolite.....	$6NaF \ Al_2F_6$	420	$3Na_2O \ Al_2O_3$	282

6. CALCULATION OF EMPIRICAL FORMULA FROM BATCH WEIGHTS

The calculation of the empirical formula of an enamel from the batch weights of the raw materials is made similarly to the calculation from analysis. In the following calculations the weight of each raw material used in the batch is divided by its formula weight to obtain the molecular proportions used. This value, multiplied by the number of molecular parts of each oxide in the formula, gives the number of molecular parts of each introduced into the enamel by the given material. Summing the values obtained for each oxide from the various raw materials, and dividing through by the total molecular parts of the basic oxides (to obtain unit basic oxides or 1 RO), the empirical formula is obtained.

Material	Formula	Formula weight	Batch weight	Molecular parts
Feldspar.....	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$	556	100	$100 \div 556 = 0.18$
Flint.....	SiO_2	60	100	$100 \div 60 = 1.67$
Borax.....	$Na_2O \cdot 2B_2O_3 \cdot 10H_2O$	382	110	$110 \div 382 = .288$
Soda ash.....	Na_2CO_3	106	50	$50 \div 106 = .472$
Saltpeter.....	$(KNO_3)_2$	202	25	$25 \div 202 = .123$
Fluorspar.....	CaF_2	78	45	$45 \div 78 = .577$
Cryolite.....	$6NaF \cdot Al_2F_6$	420	20	$20 \div 420 = .048$
Zinc oxide.....	ZnO	81	5	$5 \div 81 = .062$
Antimony oxide.....	Sb_2O_3	287	20	$20 \div 287 = .070$

The molecular proportions of oxides resulting is as follows:

Molec- ular parts	Raw material	Formula	K ₂ O	Na ₂ O	CaO	ZnO	Al ₂ O ₃	B ₂ O ₃	Sb ₂ O ₃	SiO ₂	F
0.180	Feldspar.....	K ₂ O.Al ₂ O ₃ .6SiO ₂ ..	0.18	0.18	1.08
1.670	Flint.....	SiO ₂	1.67
.288	Borax.....	Na ₂ O.2B ₂ O ₃ .10H ₂ O	0.288	0.576
.472	Soda ash.....	Na ₂ CO ₃472
.123	Saltpeter.....	(KNO ₃) ₂123
.577	Fluorspar.....	CaF ₂	0.577	1.154
.048	Cryolite.....	6NaF.Al ₂ F ₆ = 3Na ₂ O.Al ₂ O ₃ .12F.144048576
.062	Zinc oxide.....	ZnO.....	0.062
.070	Antimony oxide	Sb ₂ O ₃	0.070
Molecular parts of basic oxides.....			.303	.904	.577	.062	.228	.576	.070	2.75	1.730

The sum of the molecular parts of basic oxides = 1.846 = value to be used as divisor.

The empirical formula of this enamel is

$$\begin{array}{r}
 \left. \begin{array}{l}
 0.163 \text{ K}_2\text{O} \\
 .490 \text{ Na}_2\text{O} \\
 .313 \text{ CaO} \\
 .034 \text{ ZnO}
 \end{array} \right\} 0.124 \text{ Al}_2\text{O}_3 \left\{ \begin{array}{l}
 1.490 \text{ SiO}_2 \\
 .312 \text{ B}_2\text{O}_3 \\
 .937 \text{ F} \\
 .038 \text{ Sb}_2\text{O}_3
 \end{array} \right.
 \end{array}$$

1.000

7. CALCULATION OF BATCH WEIGHTS FROM THE EMPIRICAL FORMULA

In outlining a series of experiments for the purpose of studying enamels with reference to the effect of some one ingredient or a number of ingredients, the empirical formula has been found useful by certain investigators. It is of importance, therefore, to know how to figure batch compositions from empirical formulas. The process is just the reverse of that of figuring formulas from batch weights. The only point likely to lead to confusion is the fact that the same oxide can be derived from several different raw materials, and care must be exercised in selecting the raw materials to use. The following examples illustrate the procedure:

Given the formula of an enamel, to calculate the batch weights.
Formula:

$$\begin{array}{r}
 \left. \begin{array}{l}
 0.09 \text{ K}_2\text{O} \\
 .62 \text{ Na}_2\text{O} \\
 .10 \text{ CaO} \\
 .10 \text{ BaO} \\
 .09 \text{ ZnO}
 \end{array} \right\} 0.20 \text{ Al}_2\text{O}_3 \left\{ \begin{array}{l}
 1.60 \text{ SiO}_2 \\
 .50 \text{ B}_2\text{O}_3 \\
 1.52 \text{ F} \\
 .10 \text{ Sb}_2\text{O}_3
 \end{array} \right.
 \end{array}$$

1.00

Evidently the K_2O can be obtained from feldspar or KNO_3 ; the Na_2O can be obtained from soda ash, borax, cryolite, sodium nitrate, soda feldspar, etc.; the CaO from $CaCO_3$, CaF_2 , $CaSO_4$, etc.; Al_2O_3 from feldspar, clay, or cryolite; B_2O_3 from borax or boric acid. From this it will be seen that there is considerable freedom in choice of raw materials to obtain the final result. It is therefore necessary to first decide what raw materials are to be used in making the enamel. The following assumptions are made: All B_2O_3 is to be derived from borax; all K_2O from feldspar, assumed to be pure orthoclase; all F from fluorspar and cryolite; all CaO from fluorspar; all BaO from barium carbonate; ZnO from zinc oxide; Sb_2O_3 from antimony oxide. Flint and clay will be used if necessary to fulfill the requirements for Al_2O_3 and SiO_2 .

For convenience the calculations are arranged in tabular form. The amount of oxide added by each ingredient of the batch is subtracted from the required amount in the column for the oxide, and the difference indicates further requirements to be obtained from other sources. The weight of each raw material used is the product of the molecular parts used times its formula weight and is recorded in the column of batch weights.

Formula										Material used	Molecular parts	Formu- la weight	Batch weight
K ₂ O	Na ₂ O	CaO	BaO	ZnO	Al ₂ O ₃	SiO ₂	B ₂ O ₃	F	Sb ₂ O ₃				
0.09 .09	0.62	0.10	0.10	0.09	0.20 .09	1.60 .54	0.50	1.52	0.10	Feldspar, K ₂ O, Al ₂ O ₃ , 6SiO ₂	0.09	×556	50.04
					.11	1.06							
	.25						.50			Cryolite, 6NaF, Al ₂ F ₆11	×420	46.20
	.37 .33				.11		0		1.32				
	.04				0			.20	.20	Barium Carbonate, BaCO ₃10	×197	19.70
		.10											
		0						0		Antimony oxide, Sb ₂ O ₃10	×287	28.70
					.09								
					0				1.06	Sodium nitrate, (NaNO ₃) ₂04	×170	6.80
	.04												
322.39													

It is entirely possible to make up the same formula by use of other raw materials than those selected here. The selections will depend upon the materials available, and in some cases it may be found impossible to compound an enamel of given composition from those at hand. In such a case it will, of course, be necessary either to change the formula or to obtain other materials by which the requirements may be fulfilled.

The methods of calculation illustrated refer to the frit only. While the enamel frit is a more or less homogeneous glass, and variations in the formula of the frit represent variations in its physical character, the raw materials added to it seldom become thoroughly combined with it during the burning of the ware. While the formula of the finished enamel is sometimes given, there is seldom any gain in recasting the formula for the purpose of including in it the raw materials added in the mill. When it is desired to reproduce a steel enamel from the formula, it is generally safe to assume that all the tin oxide was added raw and that sufficient of the alumina and silica of the formula came from raw clay to amount to about 8 per cent clay at the mill. All other ingredients of the formula can be assumed as fritted without any appreciable error being introduced. While some of these might have been added raw, the amount will be so small as to be negligible so far as reproduction of the formula is concerned.

Obviously, special cases may arise where this assumption can not be safely made, for instance, in the case of many colored enamels where coloring oxides are added in the mill. In such cases the color obtained will be quite different when the coloring oxide is fritted. In the reproduction of any color, experience and experiments are necessary.

8. USE OF CURVES IN CALCULATING FORMULAS FROM BATCH WEIGHTS

A brief survey of the above outline of methods of calculating the empirical formula is sufficient to convince one of the justice of the criticism that it is a laborious process. The accompanying set of curves (Figs. 8, 9, 10, 11) greatly simplify the use of empirical formulas. By the use of these curves the work required to figure the formula is exactly the same as that required to figure the percentage composition. Likewise the work of calculating the batch weights from the formula is exactly the same as that required to figure the batch weights from the percentage composition of the oxides.

These curves are obtained by making the arithmetical calculation necessary to determine one point and then drawing a straight line through the point determined and zero.

Thus, to find the curve for formula weights of B_2O_3 , from borax ($Na_2O \ 2 \ B_2O_3 \ 10 \ H_2O$), formula (molecular) weight 382:

Assume 100 borax: $100 \div 382 = 0.262$ formula weight of borax. One formula weight of borax gives 2 formula weights of B_2O_3 .

$$0.262 \times 2 = 0.524 \text{ formula weight } B_2O_3 \text{ from 100 borax.}$$

To draw the curve: On the horizontal line representing 100 raw material, run across to the vertical line corresponding with 0.524 formula weight of oxide. Draw a straight line through this point and zero. By a simple calculation of this kind a curve for any raw material may be obtained.

To illustrate the use of these curves for calculating the formula from the batch weights of an enamel, the same composition will be used as in illustrating the use of the preceding curves (Fig. 7). The method employed is the same. Following the horizontal line corresponding to the weight of a material to the right until it intersects the curve for one of the oxides obtained from the substance, and dropping vertically to the base of the diagram, the corresponding molecular proportion of that oxide is obtained.

Molecular Parts of Oxides

Material	Weight	K_2O	Na_2O	CaO	Al_2O_3	SiO_2	B_2O_3	F	SnO_2
Feldspar.....	178	0.32			0.32	1.92			
Flint.....	140					2.344			
Borax.....	83		0.219				0.438		
Soda ash.....	15		.142						
Saltpeter.....	16	.08							
Fluorspar.....	10.5			0.136				0.27	
Cryolite.....	59.5		.426		.142			1.70	
Tin oxide.....	34								0.225
Total.....		.40	.787	.136	.462	4.264	.438	1.97	.225
Dividing by 1.323.....		.320	.595	.103	.349	3.223	.331	1.49	.170

The empirical formula is then written

$$\left. \begin{array}{l} 0.302 \ K_2O \\ .595 \ Na_2O \\ .103 \ CaO \end{array} \right\} 0.349 \ Al_2O_3 \left\{ \begin{array}{l} 3.223 \ SiO_2 \\ .331 \ B_2O_3 \\ .170 \ SnO_2 \\ 1.490 \ F \end{array} \right.$$

In order to facilitate the reading of these curves, as in the preceding set, it is sometimes necessary to use larger quantities than

those given in the batch. The weight given is multiplied by a convenient factor, which is, of course, used as a divisor of the quantity of oxide obtained from the curve.

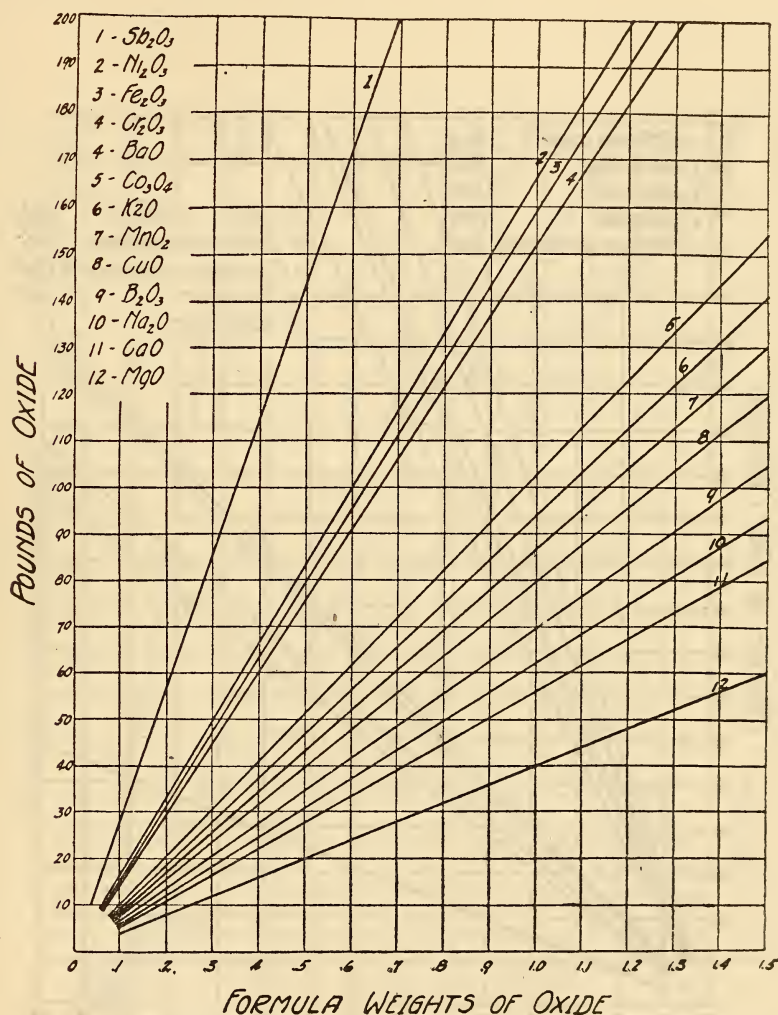


FIG. 8.—Chart for obtaining formula weights of oxide from pounds of oxide

The molecular proportions of the oxides obtained from the batch weights are divided, as in preceding calculations, by the sum of the values for the basic or RO oxides, to get the formula in standard form, unit RO.

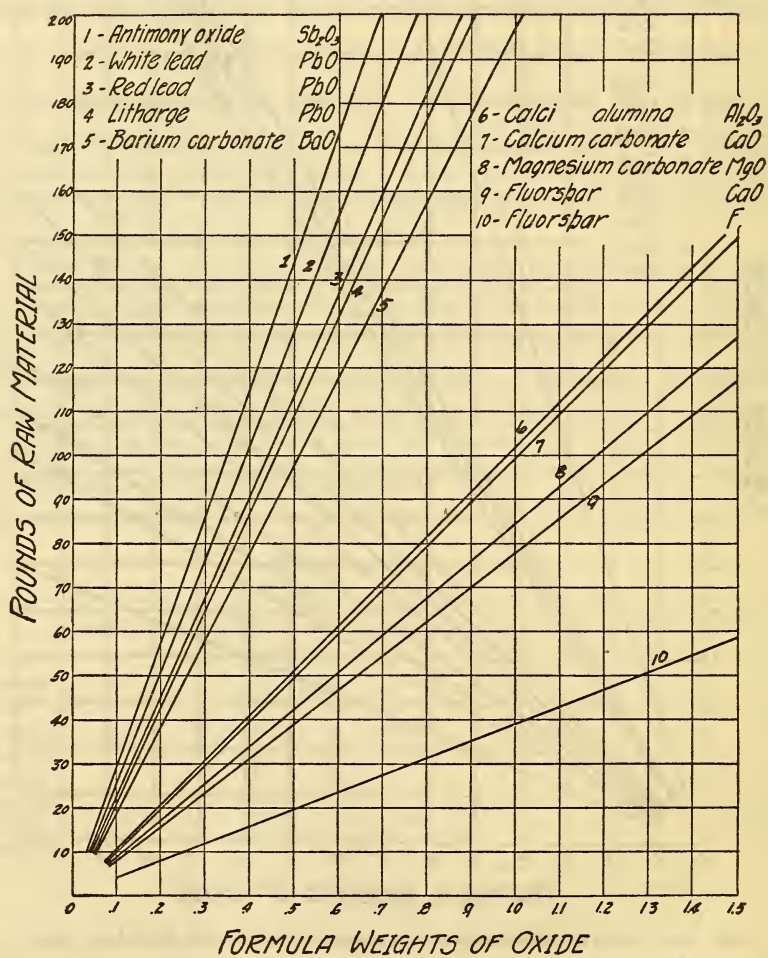


FIG 9.—Chart for obtaining formula weights of oxide from pounds of raw material

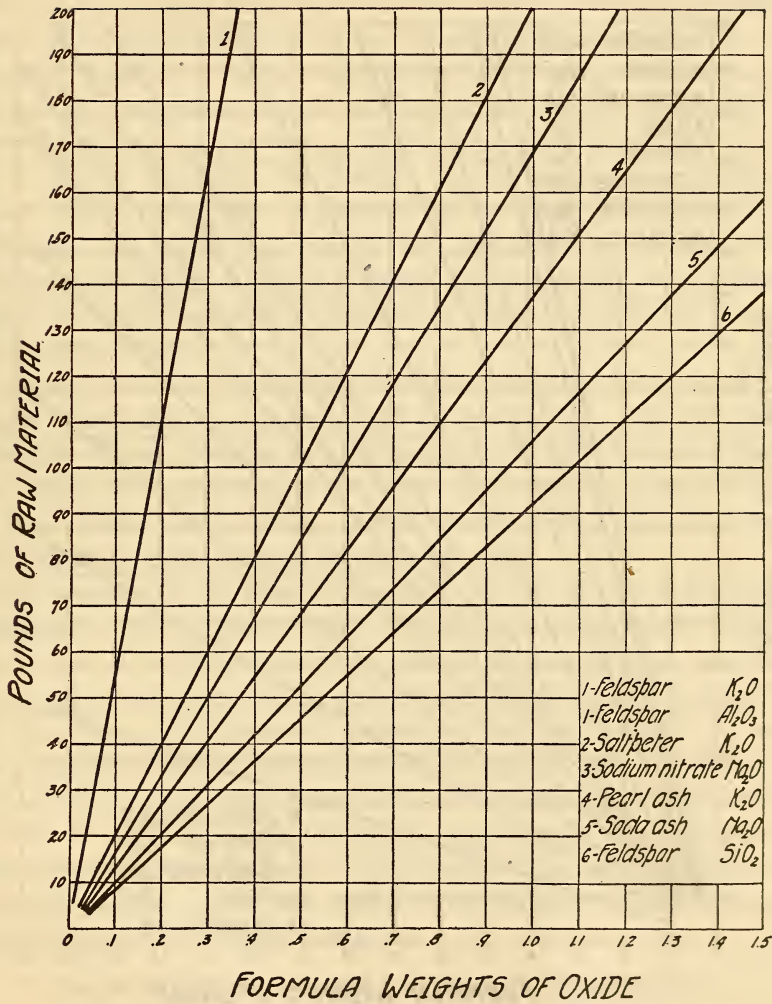


FIG. 10.—Chart for obtaining formula weights of oxide from pounds of raw material

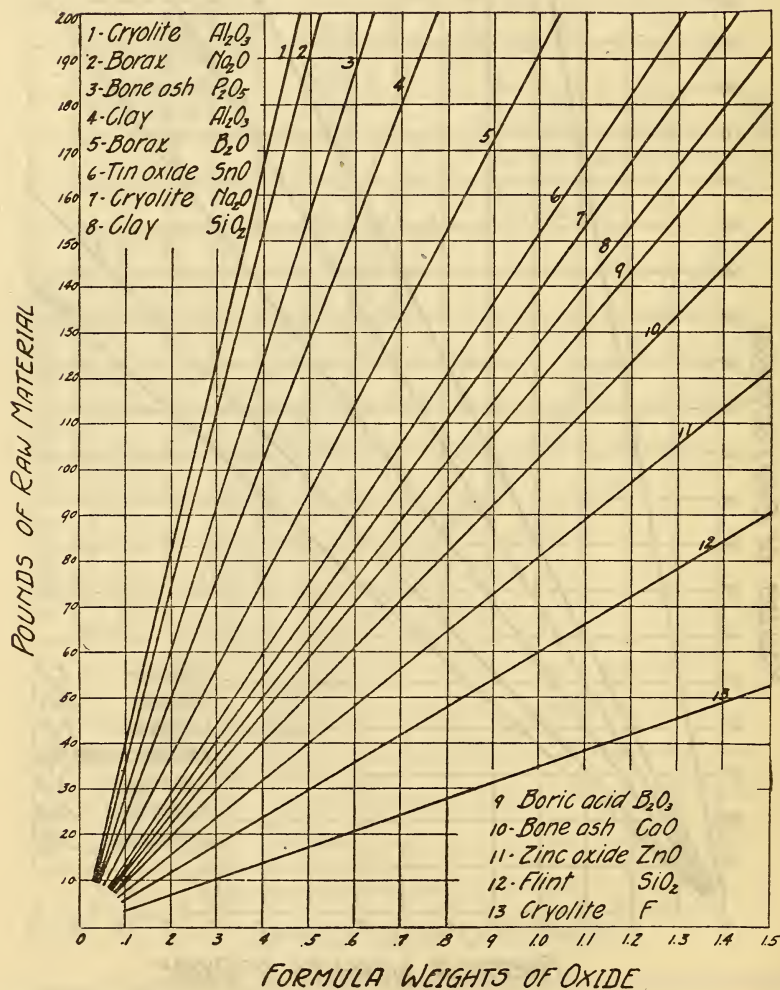


FIG. 11.—Chart for obtaining formula weights of oxide from pounds of raw material

VII. PHYSICAL PROPERTIES OF ENAMELS

1. INTRODUCTION

Articles are made of enameled iron for a great variety of purposes. In all cases it is the function of the enamel to protect the iron from corrosion. This may be its only function, as, for instance, in the case of enameled-steel articles for chemical purposes, where all other considerations are of negligible importance. On the other hand, the enamel sometimes has to perform the double function of protecting the iron from corrosion and imparting a desirable surface to the ware while subjected to treatment which has a strong tendency to destroy it. Enameled-iron cooking utensils fall in this class. A piece of ware used in the kitchen must withstand the solvent action of hot solutions, sometimes acid, sometimes alkaline, and the average housewife will soon discard it after it acquires a soiled appearance which she can not remove with scouring soap.

Another class of ware is that in which the chief function of the enamel is to impart a desired finish to the surface. In this class, while the enamel does necessarily protect the iron from corrosion, the ware is not subjected to such strong corroding agencies as in the two classes given above. As representative of this class may be mentioned reflectors and advertising signs.

The function of the iron in all cases is to serve as a support for the enamel. The primary object in making enameled-iron articles is to obtain a very strong article with little weight, such as is obtained with steel, but having surface properties such as are exhibited by glass. It is evident, therefore, that an enamel for any given purpose must possess physical properties which will enable it to withstand the destructive action of the agencies with which it comes in contact. These physical properties of the enamel are, like those of glass, influenced very greatly by its ultimate chemical composition; but there are many other factors vitally affecting the quality of the enameled ware.

2. RESISTANCE TO SUDDEN CHANGE OF TEMPERATURE

The ability of enamel to withstand sudden changes of temperature is one of the important properties of enameled wares. The ordinary enameled pan is continually subjected to hard usage in the kitchen, such as boiling dry and immediately running cold water into it.

Professor Staley in his very excellent article on "Cause and Control of Crazeing in Enamels on Cast Iron"¹⁹ says:

Three coördinate factors must always be acting to affect the fit of an enamel coat on an iron casting: (1) Difference in coefficient of contraction and expansion of the iron and enamel; (2) the strength of the enamel, which is largely dependent upon proper attachment to the iron; (3) elasticity (ductility) of the enamel, which is largely dependent upon a thin and uniform coat.

With these statements the writer is in full accord. They apply equally well to cast-iron and steel enamels.

The first of these three factors is quite generally recognized and is ordinarily thought to be the most important factor governing the toughness of enamel. The last two are equally important. Every enameler knows that a thin enamel will stand far more rough treatment than a heavy one. A piece of thin steel with a thin coat of enamel can be bent through a comparatively sharp angle and straightened out again without any rupture of the enamel visible to the naked eye. Imagine a sheet of glass, of even the same thickness as the enamel, receiving the same treatment. It will break before it has bent through any perceptible arc. Whence this difference? It lies in the ductility (elasticity) of the enamel coating and the support given by the steel base. This great elasticity, together with high tensile strength of the enamel coating, resulting from the combined tensile strength of the frit and its strong bond to the steel, is the most important factor in producing tough enamels and ware which stands severe treatment, such as abrasion and sudden changes in temperature.

Winkelmann and Schott's²⁰ investigations throw some light on the relation between chemical composition and physical properties of glass. Table 5 shows some of the values determined for different oxides, expressing their relative effect upon the physical properties.

The glasses from which these values were determined were of much more simple composition than the average enamel. It is not certain, therefore, how well the factors would apply to enamels. They do have value, however, in indicating the relative effects of the different oxides on specific physical properties, and a general idea may be obtained as to what oxides are most efficient in producing a desired physical property. It may be noted in this connection that glasses of high density show high luster. The figure for B_2O_3 is an exception in this respect when applied

¹⁹ Staley, H. F., *Trans. Am. Ceram. Soc.* 14, p. 530; 1912.

²⁰ Hovestadt, *Jena Glass*.

to enamels. The effects of the various oxides on tenacity and elasticity is worthy of note in connection with enamel compositions.

TABLE 5.—Coefficients for Mechanical Properties of Glasses

	Density	Coefficient of elasticity ^a	Crushing strength	Tensile strength
SiO ₂	2.3	70	1.23	0.09
B ₂ O ₃	1.9	60	.90	.065
ZnO.....	5.9	100	.60	.15
PbO.....	9.648	.025
BaO.....	7.0	70	.05	.05
CaO.....	3.3	70	.20	.20
MgO.....	3.8	40	1.10	.01
K ₂ O.....	2.8	70	.05	.01
Na ₂ O.....	2.6	100	.02	.02
Al ₂ O ₃	4.1	150	1.00	.05
P ₂ O ₅	2.5576	.075
As ₂ O ₅	4.1	40	1.00	.03

^a Factors for borosilicate glasses free from PbO and P₂O₅.

By use of these factors values were calculated for glasses by the formulas

$$\frac{100}{S} = \frac{a_1}{z_1} + \frac{a_2}{z_2} + \frac{a_3}{z_3} + \dots$$

$$E = a_1x_1 + a_2x_2 + a_3x_3 + \dots$$

$$P = a_1y_1 + a_2y_2 + a_3y_3 + \dots$$

S = specific gravity of the glass;

E = coefficient of elasticity of the glass;

P = tensile or crushing strength of the glass;

$a_1a_2a_3$ = percentages of various oxides in the glass;

$z_1z_2z_3$ = density factors for various oxides;

$x_1x_2x_3$ = coefficient of elasticity factors;

$y_1y_2y_3$ = tensile or crushing strength factors.

3. RESISTANCE TO ABRASION

The ability of enamels to withstand abrasion depends largely upon the same properties as their ability to stand sudden changes in temperature. If enamels are so constituted as to be able to stand the latter they will probably also stand the former. Recapitulating, we may say that toughness is imparted to enamel by (1) proper union of the enamel to the steel and proper union of the different coats of enamel, (2) the use of as thin a coating of enamel as circumstances will permit, (3) making the frit of such a composition as to have high elasticity and tensile strength.

4. CONTROLLING THE TOUGHNESS OF ENAMELS

Toughness, as applied to steel or sheet-iron enamels, is understood to mean the ability to withstand impact or flexure. (1) The first and most important precaution to take in controlling this property is to *keep all enamels thin*. (2) The heavier the steel the tougher the ware. (3) Places where there is double thickness of steel due to lapping parts riveted or welded on necessitate special care in dipping and burning. A thinner or more fusible enamel on such parts, where practicable, makes for better quality. (4) Sharp angles should be avoided. (5) Do not grind enamel too finely. Ground coat especially should be quite gritty when applied; 60-mesh is fine enough, 100-mesh is too fine. (6) Overburning is better than underburning; either will destroy toughness if carried to extremes. (7) Sudden cooling by exposure to draft of air or setting ware on cold surface makes brittle ware. (8) Metallic oxides add toughness to enamel, especially Co_3O_4 , Ni_2O_3 , CuO , MnO_2 , PbO , and Fe_2O_3 . (9) The formula of the enamel should be well balanced in all respects, due regard being paid to those articles which add elasticity and tensile strength. In reference to this it must be remembered the elasticity and toughness of the finished product are influenced quite as much by the manipulation of the enamel as by its composition. ZnO , Al_2O_3 , SiO_2 , CaO , BaO , and B_2O_3 all are valuable ingredients, but the properties of the enamel depend far more upon the ratios between them than upon the influence of any one individually. (10) Use caution in adding raw material at the mill. A little magnesia is good; 6 to 10 per cent clay is sufficient. A little raw flint sometimes is valuable. (11) Fluorides are undesirable. In large amounts they make poor enamels. A white enamel depending largely on fluorides for opacity is very likely to be of poor quality so far as toughness is concerned. (12) Strict attention to every detail in the process of manufacture is absolutely essential.

VIII. RESISTANCE OF ENAMELS TO CHEMICAL ACTION

1. INTRODUCTION

The ability of enamels to resist corrosion by the chemical action of water and of solutions which come in contact with them depends primarily upon the ultimate chemical composition of the surface exposed to these solvents, but of no less importance is the degree to which the material approaches a homogeneous glass. The higher the percentage of unfritted materials added to the enamel, the greater the danger of destruction by chemical action.

Enamels for sheet steel are generally applied by dipping or spraying, and this requires the addition of certain raw materials to the frit in order to get the enamel properly applied. White enamels require an addition of an opacifier, such as tin oxide or a substitute, in addition to raw clay for floating the frit, and a flocculating agent, such as borax or other salts. In view of the fact that these enamels are burned in from two to four minutes, it is very evident that complete chemical union of these raw materials with the frit can not be obtained. It follows, therefore, that the finished enamel is always composed of the frit carrying in suspension either the raw material as added or some compound of the frit with the raw material, representing a partially completed reaction and a conglomerate mixture of materials, far from homogeneous and very unlike a clear glass, such as glass vessels are made of.

2. ACTION OF GLASS

Experiments performed by Schott, Foerster, and Mylius²¹ have shown how susceptible even high-grade glass is to the chemical action of water. They show that the solvent action does not proceed directly, as water dissolves sugar, but that the glass surface absorbs water from the air or solution in contact with it. The process of solution, resulting in the passage from solid glass to dissolved substance, is affected through a series of intermediate transformations. They note that water glass and other glasses containing little lime are especially susceptible to this solvent action. This citation emphasizes the importance not only of the ultimate chemical composition, but also of the thoroughness with which the enamel is melted to a homogeneous mixture. It is obvious that soluble salts and especially alkalis should not be added in large amounts in the mill if enamels are to be subjected to destructive chemical agencies.

Foerster's conclusions, as a result of experiments on the solubility of many types of glass, are summarized as follows:

1. The total alkalis in glass have a marked effect upon its power to resist corrosion by water.
2. In good glasses it is immaterial whether potash or soda is the source of the alkali.
3. Boric acid in combination with silicic acid seems to check solution.

Kohlrausch²² tested a number of glasses for solubility in water and concluded that solubility is mainly determined by the gross

²¹ Hovestadt, *Jena Glass*, p. 320.

²² Hovestadt, *Jena Glass*, p. 349.

content of alkali. Potash, however, appeared more conducive to solubility than soda.

Walker and Smither²³ have recently made solubility tests on various brands of chemical glasswares. The analyses of the glasses are shown in Table 6.

TABLE 6—ANALYSES OF CHEMICAL GLASSWARE

Ware	Kavalier beaker	M. E. G. Co. beaker	Pyrex beaker	Jena beaker	Jena flask	Nonsol beaker	Fry beaker	Libbey beaker
Al ₂ O ₃	0.14	1.0	2.0	4.2	4.2	2.5	2.7	2.1
Fe ₂ O ₃	0.08	0.35	0.25	0.25	0.27	0.23	0.22	0.44
ZnO.....		5.6		10.9	10.9	7.8	3.6	
PbO.....								1.0
MnO.....	0.02	0.02	0.01	0.01	0.01	0.01	0.03	0.03
CaO.....	8.7	0.66	0.29	0.63	0.56	0.79	2.6	0.42
MgO.....	0.17	4.3	0.06	0.21	0.25	3.4	2.6	0.08
Na ₂ O.....	7.1	10.8	4.4	7.5	7.8	10.9	9.8	8.2
K ₂ O.....	7.9	0.30	0.20	0.37	0.31	0.30	1.5	0.67
SiO ₂	75.9	73.0	80.5	64.7	64.7	67.3	68.6	75.9
B ₂ O ₃		3.6	11.8	10.9	10.6	6.2	8.1	10.8
P ₂ O ₅	0.08							
SO ₃	0.20	0.02						
As ₂ O ₃	Trace	0.02	0.70	0.14	0.19	Trace	0.18	0.36
Sb ₂ O ₃		0.60				0.62		
Total.....	100.29	100.27	100.21	99.81	99.79	100.05	99.93	100.00

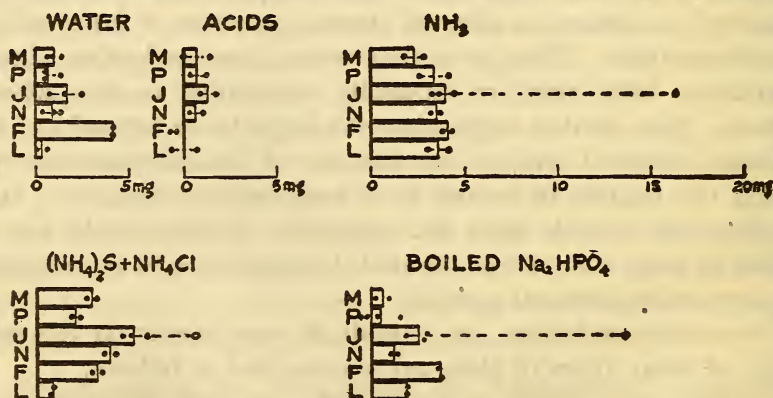


FIG. 12.—Loss in weight of flasks with water, acids, ammonia, ammonium sulphide and chloride, and sodium-phosphate solutions

The glasses were subjected to the action of boiling water and various acid and alkaline solutions, and the loss of weight was determined with care.

The results are shown in Figs. 12 and 13, in which the letters K, M, P, J, N, F, and L indicate Kavalier, M. E. G. Co., Pyrex, Jena, Nonsol, Fry, and Libbey,

²³ B. S. Tech. Paper, No. 107, Comparative Tests of Chemical Glassware.

respectively. In these figures individual accepted determinations are shown by dots; determinations which are believed in error, and therefore omitted from the averages, are indicated by circles. The length of the rectangles indicates averages of the accepted values.

Cowper,²⁴ who noted that solutions of ammonium sulphide and chloride attacked glass more vigorously than sodium carbonate, must have used glass very different from the ware tested here.

Table 7 gives a general summary of the resistance to the various solutions and to mechanical and heat shocks of the wares tested. In this table the numerical

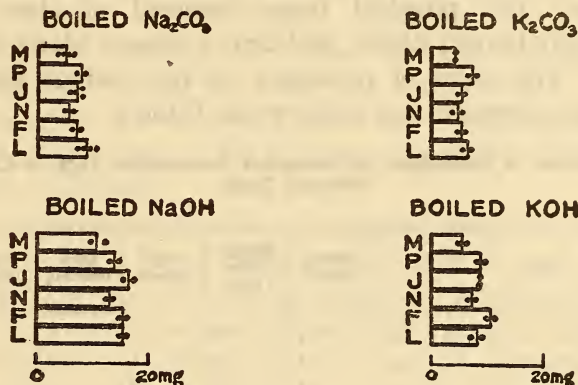


FIG. 13.—Loss in weight of flasks with sodium carbonate, potassium carbonate, sodium hydroxide, and potassium hydroxide solutions

subscripts indicate the minor differences in resistance, the lowest number being the most resistant. The absence of a subscript indicates that the differences in resistance are too small to justify any differentiation between the wares graded in the same group. In the rating of resistance to caustic alkalis the boiling tests only have been considered.

TABLE 7

Ware	Resistance to—						
	Water	Mineral acids	Carbonated alkalis	Caustic alkalis	Ammonia and ammonium salts	Heat shock	Mechanical shock
Kavalier.....	Poor.....	Good.....	Poor.....	Good 2....	Good 2....	Poor.....	Poor
M. E. G. Co.....	Good 3....	...do....	Good 1....	...do.1....	...do....	...do....	Do.
Pyrex.....	...do.3....	...do....	...do.3....	Fair.....	...do....	Good 1....	Good ^a
Jena.....	...do.4....	...do....	...do.2....	...do....	...do....	...do.3....	Fair
Nonsol.....	...do.3....	...do....	...do.1....	...do....	...do....	...do.2....	Do.
Fry.....	...do.4....	...do....	...do.2....	...do....	...do....	Poor.....	Good
Libbey.....	...do.1....	...do....	...do.3....	...do....	...do....	Good 2....	Do.

^a Far superior to any of the other wares.

3. WORK OF ORTON

Prof. Edward Orton, jr., has reported²⁵ the results of tests on three makes of enameled-steel automobile tags. The tags

²⁴ Jour. Chem. Soc., 41, p. 254; 1882.

²⁵ Jour. Am. Ceram. Soc., 11, pp. 320-341.

were subjected to the following chemical tests: Boiling in water for 8 hours; boiling in 1 per cent sulphuric acid for 15 minutes; exposure to acid fumes by being kept for 18 hours in a bell jar in which a beaker of strong hydrochloric acid was sitting. The relative order of resistance of the three makes of enameled ware was the same in these three tests. Boiling in dilute sulphuric acid proved the most severe test, and boiling in water the next in severity. The physical tests consisted of slow bending, repeated light impact blows, and heavy impact blows of increasing force. The order of resistance to the various tests of the three lots of enameled tags is shown in Table 8.

TABLE 8.—Order of Resistance of Enameled Automobile Tags to Chemical and Physical Tests

Lot	Boiling water	Boiling dilute acid	Acid fumes	Slow bending	Light impact	Heavy impact
1.....	2	2	2	1	3	1
2.....	1	1	1	3	1	3
3.....	3	3	3	2	2	2

Prof. Orton's conclusions on the results of the above tests are as follows:²⁶

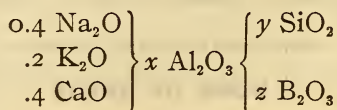
1. Wide differences are found in solubility, either in water, or dilute acids, or even acid fumes, between enamels of apparently equal quality.

2. No correlation can yet be shown between chemical-resisting properties and physical strength or beauty of appearance and finish. It seems as if excellence in several directions might be possessed by one and the same piece of enameled metal, but there is no causal relationship between these various kinds of excellence and it is much more likely that any single piece will be deficient in one or more directions.

4. WORK OF SHAW—FIRST INVESTIGATION

A study of the relation of chemical composition to the resistance to acid corrosion as well as tests to determine the resistance to sudden temperature changes was made by the writer on a large number of white enamels.²⁷

The formula selected as a basis for the investigation was as follows:

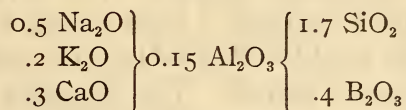


x , y , and z were variables, the RO remaining constant. This RO is a little higher in CaO than the average of white enamels, but it

²⁶ Trans. Am. Ceram. Soc., 11, p. 335.

²⁷ J. B. Shaw, Trans. Am. Ceram. Soc., 12, pp. 463-494.

was made so in order to insure any of the enamels against solubility because of the RO. The average white enamel formula is about as follows:



Of course, there are many variations in composition which this does not include, some formulas containing P_2O_5 , Sb_2O_3 , PbO , BaO , and ZnO , but they are rather the exception than the rule. In the enamels tested the SiO_2 was varied from 1.083 to 4.53 molecular parts; the SiO_2 - B_2O_3 ratio was varied from 3:1 to 7:1, and the alumina from 0.1 to 0.4 molecular parts. In all 120 compositions were made.

The test pieces used were rectangular pieces of 26-gage steel, $1\frac{1}{2}$ by 3 inches. Each sample was coated on both sides with a reliable ground coat, care being taken in coating and burning to see that the edges remained coated with enamel. Seven samples were coated with each enamel, two coats of white being applied to each sample on both sides.

The time and temperature of burning were varied to suit the different enamels. Some enamels required high temperature and longer time in the muffle than others. The object was to produce the very best piece of ware that could be produced with each enamel. The temperature used for burning varied from 1500 to 1800° F, increasing with increase of SiO_2 and Al_2O_3 and decrease of B_2O_3 .

For testing these enamels two acids were used in order to compare the results. A sample of each enamel was boiled for 15 minutes in a 1 per cent solution of H_2SO_4 and the operation repeated on a new sample for accuracy. Another sample of each enamel was boiled for 20 minutes in a 75 per cent solution of acetic acid and the operation repeated on a new sample.

After having weighed each sample accurately to 0.001 g, they were placed in a vessel of distilled water and the water heated to boiling. The H_2SO_4 solution, having been accurately measured to make a 1 per cent solution of acid, using distilled water and concentrated acid, was also heated to boiling. The samples were then taken out of the boiling water and placed in the boiling acid. This precaution was taken in order to insure no loss in weight from the enamel peeling off because of cold samples being thrown in boiling acid. As soon as the samples had boiled for 15 minutes they were placed in hot water, and cold water was run in to

insure gradual cooling. They were then thoroughly washed in distilled water by gentle rubbing with a soft cloth. After drying, they were again accurately weighed. The difference in weight represented loss due to solution. Each sample having an area of 9 square inches, the total loss divided by 9 represented the loss per square inch of exposed surface. The operation with the acetic acid was exactly the same as with the H_2SO_4 .

Comparison of the resistance of enamels to acid treatment has at times been based on the percentage of weight lost by enameled pieces when subjected to the same acid treatment. It seems quite obvious that this basis for comparison is wrong and will lead to contradictory results. For instance, suppose we have two pieces of ware, both containing the same surface area, one of 18-gage steel with a ground coat, two coats of white, and a coat of blue, all heavy coats. The other 20-gage, but all light coats of enamel. Obviously, the latter piece will be much the lighter of the two. Now if the same enamel is used on each piece of ware, it is likely that on going through the same acid treatment the actual amount dissolved will be practically the same, but the percentage of weight lost will be quite different. Hence, it seemed that it would be more accurate to base this comparison on the absolute loss per unit of exposed area.

The following statements may be made in reference to the solubility of the enamels in sulphuric acid:

1. Everything else being constant, the solubility decreased directly as the SiO_2 increased.
2. Everything else being constant, the solubility decreased as the content of Al_2O_3 increased.
3. Everything else being constant, the solubility decreased as the B_2O_3 decreased.
4. The three foregoing statements may be summed up in the one—that the solubility decreased as the enamels became more refractory.

5. When the enamels became too refractory they were unusable on account of tendency to chip off and failure to develop gloss during burning.

The results of the acetic acid test were not so sharply defined as in the H_2SO_4 test, but in general the statements made concerning solubility in H_2SO_4 also hold true with regard to acetic acid. One fact was quite clearly shown; namely, 75 per cent solution of acetic acid has very much less solvent action on enamels than has a 1 per cent solution of H_2SO_4 . This was indicated, not

only by the very low loss per square inch in weight, but by the fact that so many samples retain their gloss after the acetic acid treatment, while none of the enamels showed any gloss after H_2SO_4 treatment. The gloss was affected to some extent on all samples by the acetic acid, but the effect on those high in SiO_2 and Al_2O_3 was very slight indeed.

5. WORK OF SHAW—SECOND INVESTIGATION

(a) ENAMELS TESTED.—A manufacturer found that his white enamel, which was giving satisfaction when used on cooking utensils, was easily destroyed by lemon juice. The series of enamels shown in Tables 9 and 10 was made in order to produce a pure white enamel with high gloss which would not be affected. The formulas are given in the order in which the enamels were made. It is not possible to arrange the series as a whole in any logical sequence as regards composition, for the list includes variations in every ingredient of the enamel. The conditions under which the work was done precluded the possibility of covering entirely the field of possible compositions, since this was a factory problem requiring quick solution. The method of attack consisted in making up and testing a series of enamels, then preparing another series on the basis of information obtained from the first. The formulas given are for the frits only. In some cases no raw material other than clay was added. All variations in the material added at the mill are stated in discussing the results.

(b) RESULTS OF ACID TESTS.—Each enamel was applied to steel and then tested with lemon juice, which contains about 7 per cent citric acid, a standard 10 per cent solution of citric acid, and also a 10 per cent solution of oxalic acid. Each test consisted in washing the ware thoroughly with soap and water, drying it, and dropping the solution on the surface. The solution was left on the ware for different periods—10 minutes, 30 minutes—and some was allowed to evaporate to dryness.

Examination of the original formula shows it to be about average white enamel in all respects. This enamel was readily attacked by the lemon juice and other acid solutions. The 10-minute treatment left a distinct rough spot, while the 30-minute treatment produced a very rough spot.

Enamel 1 took a stain when treated with 10 per cent citric acid. It did not lose its gloss readily, but the iridescent stain left after two hours' treatment is characteristic of all enamels which are attacked by acid. It is the first indication of

attack, which is followed by dullness, loss of gloss, and finally rough, uneven surface. Enamel 2 lost its gloss when tested with acid.

TABLE 9.—Formulas of Enamels

	K ₂ O	Na ₂ O	CaO	MgO	PbO	BaO	ZnO	Al ₂ O ₃	SiO ₂	B ₂ O ₃	Sb ₂ O ₃	SiO ₂ B ₂ O ₃	F
Original.....	0.18	0.59	0.13	0.0	0.0	0.05	0.06	0.26	1.96	0.48	0.04	4.0	1.22
1.....	.04	.36	.20	0	0	.20	.20	.10	3.0	.40	0	7.5	.88
2.....	.34	.36	.30	0	0	0	0	.10	3.0	.40	0	7.5	1.28
3.....	.17	.58	0	0	0	.07	.18	.19	1.75	.30	.07	5.8	.48
4.....	.27	.65	.08	0	0	0	0	.20	1.20	.24	0	5.0	1.24
5.....	.30	.30	0	.13	0	.13	.13	0	2.00	0	0	0
6.....	.30	.30	0	0	0	.20	.20	0	2.00	0	0	0
7.....	.13	.57	0	.30	0	0	0	0	1.65	.40	0	4.1	0
8.....	.30	.30	0	.13	0	.13	.13	0	2.0	0	0	0
9.....	.30	.30	0	.13	0	.13	.13	0	2.0	.10	0	20.0	0
10.....	.30	.30	0	0	.13	.13	.13	0	2.0	0	0	0
11.....	.30	.43	0	0	0	.13	.13	0	2.0	0	0	0
12.....	.30	.40	0	.03	0	.13	.13	0	2.0	0	0	0
13.....	0	.31	0	0	.28	.14	.25	0	1.37	0	0	0
14.....	0	.40	0	0	.45	.16	0	0	1.65	0	0	0
15.....	0	.32	0	0	.18	.13	.36	0	1.50	0	0	0
16.....	0	.35	0	0	.15	.22	.27	0	1.90	0	0	0
17.....	0	.48	0	0	.09	.20	.24	0	1.66	0	0	0
18.....	0	.35	0	0	0	.22	.43	0	1.90	0	0	1.08
19.....	0	.55	0	0	.11	.16	.20	.09	1.27	0	0	1.08
20.....	0	.60	0	0	0	.10	.10	.09	1.50	0	0	1.20
21.....	.20	.50	0	.03	.15	.13	.13	.10	2.00	0	0
22.....	0	.35	0	0	0	.22	.27	.10	2.00	0	0	1.20
23.....	.30	.40	0	.03	0	.13	.13	.14	2.00	0	0	0
24.....	.30	.40	0	0	0	.15	.15	0	3.0	.10	0	30.0	0
25.....	.18	.28	.34	.02	0	.09	.09	.07	1.46	0	068

Enamels 3 and 4 had no lime, but both contained cryolite. No. 3 was a good soft enamel, but was easily destroyed by citric acid. No. 4 was a poor enamel and easily destroyed by citric acid.

Enamels 5 and 6 contained no lime, no fluorine, and no boric acid. These glasses were taken from Orton's Easily Fusible Glass Without the Use of Lead or Boracic Acid.²⁸ Neither of these showed any mark from citric acid, but they were too refractory to use as enamels. No. 6 was most refractory. No. 7 was an easily fusible enamel containing neither fluorspar nor cryolite, but it was easily destroyed with 10 per cent citric acid. No. 8 was slightly attacked and also was quite refractory. No. 9 was made by a slight addition of boric acid to No. 5. This slight amount of B₂O₃ caused it to be easily destroyed by citric acid, although it showed no mark when boric acid was left out.

²⁸ E. Orton, jr., Trans. Am. Ceram. Soc., 5, p. 305.

TABLE 10.—Batch Weights of Enamels

	Antimony oxide	Boric acid	Borax	Red lead	Zinc oxide	Barium car- bonate	Magnesium carbonate	Fluorspar	Salt-peter	Soda ash	Cryolite	Flint	Feldspar
Original.....	11.5	0	91.7	4.9	9.8	10	20	6.4	33.6	44.4	103
1.....	0	0	76.4	0	16.2	39.4	0	15.6	2	2	16.8	152	39.5
2.....	0	0	76.4	0	0	0	0	23.4	62	2	16.8	152	39.5
3.....	20	0	57.3	0	14.6	13.7	0	0	20	28.6	16.8	43.2	86.9
4.....	0	0	46.0	0	0	0	0	6.2	44	24.3	37.8	27	63.2
5.....	0	0	0	0	10.5	25.6	10.9	0	60	31.8	0	120	0
6.....	0	0	0	0	16.2	39.4	0	0	60	31.8	0	120	0
7.....	0	0	76.4	0	0	0	21	0	26.2	29.2	0	99	0
8.....	0	0	0	0	10.5	25.6	10.9	0	60	31.8	0	120	0
9.....	0	12.4	0	0	10.5	25.6	0	0	60	31.8	0	120	0
10.....	0	0	0	29	10.5	25.6	0	0	60	31.8	0	120	0
11.....	0	0	0	0	10.5	25.6	0	0	60	45.5	0	120	0
12.....	0	0	0	0	10.5	25.6	2.4	0	60	42.4	0	120	0
13.....	0	0	0	63	20.5	27.6	0	0	0	32.8	0	82.2	0
14.....	0	0	0	102	0	31.5	0	0	0	42.4	0	99	0
15.....	0	0	0	41	29.2	25.6	0	0	0	43.9	0	90	0
16.....	0	0	0	34	21.8	43.3	0	0	0	37.0	0	114	0
17.....	0	0	0	20	19.4	39.4	0	0	0	50.8	0	100	0
18.....	0	0	0	0	34.8	43.3	0	0	0	37.0	0	114	0
19.....	0	0	0	24	16.2	31.5	0	0	0	29.7	37.8	76.2	0
20.....	0	0	0	0	8.1	19.7	0	0	0	35.0	37.8	90	0
21.....	0	0	0	34	10.5	25.6	0	0	40	21.0	42	120	0
22.....	0	0	0	0	21.8	43.3	0	0	0	5.3	42	120	0
23.....	0	0	0	0	10.5	25.6	2.4	0	52	38	0	63.6	79
24.....	0	0	19.0	0	12.1	29.5	0	0	60	37.4	0	180	0
25.....	0	0	0	0	7.3	17.7	1.7	26.5	30	27.5	0	60	39.5

No. 10 was made by substituting PbO for MgO in No. 5. The result was the same as when boric acid was added; the desired fusibility was obtained, but the enamel was distinctly etched by one hour's treatment with 10 per cent citric acid.

No. 11 was made by replacing the MgO in No. 5 with Na₂O. Distinct improvement was noted. The fusibility increased, and the enamel was not visibly affected by 10 per cent citric acid.

No. 12 was very similar to No. 11 and was practically acid-proof. This enamel was used successfully as a glass coating over another white enamel. It was too refractory to work satisfactorily alone, but it was the best enamel obtained for the desired purpose.

Enamels 13, 14, 15, 16, and 17 were further attempts to soften the enamel by the use of PbO. None of these contained any fluorspar or cryolite. No. 14 was very much like No. 13. No. 15 was a distinct improvement over No. 14, but still took a slight iridescent stain with 10 per cent citric. Nos. 16 and 17 were easily

fusible and showed only a slight iridescent stain when exposed to 10 per cent citric acid for 12 hours. They were unaffected by 25 per cent H_2SO_4 solution boiled for 2 hours. No. 18 was similar to No. 17 in the acid test, but it was still harder than Nos. 18 or 12.

Nos. 19 and 20 were composed of 80 per cent of Nos. 12 and 16, respectively, and 20 per cent cryolite. The resultant frits were very much softer than Nos. 12 and 16, making good enamels in this respect. Both were easily destroyed by citric acid. Nos. 12 and 16 were unaffected in the same treatment.

No. 21 had the same formula as No. 12, except that No. 21 contains fluorine, while No. 12 contains none. The 0.10 Al_2O_3 in No. 21 was obtained from cryolite. No. 21 was very soft (fusible) and easily destroyed by citric acid, while No. 12 was unaffected by citric acid and was quite refractory. No. 21 was very opaque, and good as an enamel but useless for the purpose desired.

No. 22 had the same formula as No. 16, except for fluorine and the addition of 0.10 Al_2O_3 in No. 22 being as cryolite. The result here was exactly the same as with No. 21. The fusibility and opacity of No. 22 were excellent, but it is easily destroyed by citric acid.

Nos. 23 and 24 were slight modifications of No. 12 in attempting to increase its fusibility. No gain in fusibility was obtained. Neither was affected by citric acid. No. 25 was easily destroyed by acid.

Summarizing the results of these tests, the following conclusions were drawn:

1. Fluorine is decidedly detrimental to enamels which are subject to weak acid solutions. When added to enamels as fluorspar or cryolite in large or small amounts, it renders them subject to easy attack and destruction by ordinary lemon juice.

2. Boric acid in easily fusible enamels renders them easily destroyed by weak acids, such as lemon juice, but in refractory enamels it can be used in small amounts and the enamels still maintain stability against acids. This conclusion is substantiated by the Pyrex and other chemical glasswares now on the market.

3. No enamel of the borosilicate type made in this series was found proof against 10 per cent citric acid.

4. Enamels containing no fluorine or boric acid can be easily made proof against citric acid, but it was not found possible to

reduce their refractoriness to a sufficiently low point to make them satisfactory as white enamels. No. 12 was the best enamel made as far as stability against lemon juice is concerned. This is too refractory to work well as a white enamel. It can be successfully applied over a hard white enamel of inferior acid resisting properties to give the desired result.

(c) OPAQUE ENAMELS VERSUS TRANSLUCENT ENAMELS.—Upon reading the results of the above, one is likely to arrive at the conclusion that enamels sufficiently fusible to burn as enamels will be readily attacked by citric acid. While this is true of the above enamels, it must be borne in mind that these enamels were all required to be white. All first-coat enamels for sheet steel are colored blue, brown, or black, and when white enamels are applied over them the heat treatment in burning must not be too severe. White enamels of the type ordinarily used for cooking utensils will be converted to a dark gray, or even black, if the burning is sufficiently prolonged. It will be seen, therefore, that the burning of white enamels is necessarily limited to a comparatively light heat treatment. Some of the enamels given above would make very good ware if it were possible to give them sufficient heat treatment to burn them well on the ware. But if they are burned to this extent, the ware would not be white. Experience has shown that enamels which are much more refractory than any of these can be burned on steel to give a very satisfactory ware, but in no case is an enamel made white by the use of opacifiers used for highly acid-resisting ware. The results obtained in this work form a very strong argument against opaque enamels and in favor of translucent colored enamels for culinary purposes or any other use where resistance to corrosion is of importance. The same thing is true of enamels required to possess toughness to a high degree, in view of the fact that colored enamels can be made in a thin coat, while white enamel coatings must be much heavier in order to be opaque.

6. WORK OF LANDRUM

R. D. Landrum²⁹ gives the result of tests on 10 white enamels for sheet steel. Various tests were made on these, including corrosion by 20 per cent acetic acid, study of behavior during rapid expansion and contraction, brittleness, elasticity, and adhesion of enamel to the iron. The accompanying table shows a summary of the data obtained.

²⁹ Trans. Am. Ceram. Soc., 14, p. 489.

TABLE 11.—Results of Tests of 10 White Enamels

No.	Formula weights of SiO_2	Molecular ratio $\text{SiO}_2:\text{B}_2\text{O}_3$	Total alkalis, formula weights	Fluorine, formula weights	Order of solution	Sudden change of temperature	Resistance to impact
2.....	1.636	4.1	0.694	0	1	1	3
3.....	2.217	3.5	.991	0	2	3	9
4.....	2.571	9.5	.932	0.721	3	10	6
5.....	2.447	8.6	.680	.636	4	6	2
1.....	2.513	9.6	.683	.599	5	2	5
10.....	2.013	3.2	.983	0	6	5	7
9.....	2.406	7.4	.732	.834	7	8	10
6.....	1.558	3.8	.757	.452	8	7	8
7.....	2.525	9.9	.679	.598	9	9	4
8.....	1.509	3.3	.772	.215	10	4	1

Study of these data leads to the following conclusions regarding the action of these enamels in resisting corrosion by acetic acid:

1. Molecular amount of total alkalis does not materially affect the relative solubility of enamels. Indeed, with the exception of No. 2, the best enamel of the 10 is the one highest in total alkalis, the second best having 0.932 total alkalis.

2. The best enamels have no fluorine but high B_2O_3 . Two of the poorest have high B_2O_3 and low fluorine. The presence of fluorine is distinctly detrimental to the stability of the enamel, as is evidenced by Nos. 4, 5, and 6, which should be decidedly superior to 1 and 2 because of their lower content of B_2O_3 and smaller content of alkalis. No. 10 is the only member of the series which does not support this conclusion. There is nothing in the composition to indicate that this enamel should not be classed with No. 3, which is very similar to it.

3. From the author's description of the fritting and color of the enamels it seems reasonable to infer that practically all of the fluorine was driven out of 4 and 5, which lends support to the conclusion that those lowest in fluorine gave best results in the acid test, irrespective of the alkali or boric acid content.

It will be observed that there is absolutely no parallelism between chemical and physical excellence. The ability of the enamel to withstand chemical corrosion seems to bear no relation whatever to its ability to withstand impact or sudden change of temperature. A still more striking fact is that there seems to be no relation between the ability of the enamels to withstand sudden change of temperature and that to withstand impact.

7. ACTION OF VARIOUS ACIDS ON ENAMELS

The relative action on a given enamel of different acids and of various strengths of the same acid has been the subject of considerable investigation. Landrum³⁰ placed a given amount of solutions of acetic acid of various strengths in vessels of a given size and coated with the same enamel. The solutions were then evaporated to dryness on a gas hot plate. The maximum action was found to occur at about 20 per cent, by volume, of acetic acid with two enamels. The action of highly concentrated acids was almost negligible. As pointed out by Staley³¹, this is to be expected, for with this acid and method of testing the rate of solution of necessity varied according to the following factors:

1. THE DISSOCIATION OF THE ACID.—In dilute solutions the acid is more highly dissociated than in concentrated solutions.

2. THE AMOUNT OF ACID PRESENT.—Dilute solutions contain fewer units of acid.

3. THE RATE OF EVAPORATION.—The concentration of the acid solutions varied continuously as they were boiled, the water being evaporated first and the acid solution becoming more and more concentrated. Therefore, the more dilute the acid the longer the time during which active concentrations were acting. It also follows that the slower the rate at which the acid is concentrated the greater will be its solvent action.

Poste³² has tested the relative action of various strengths of acetic, hydrochloric, nitric, and sulphuric acids on grains of enamel. In his first investigation he used grains passing a certain size sieve gauze. In the second he used accurately sized grains in order to avoid differences in action due to increase of surface area with increased size of grains. The results obtained were similar to those of Landrum. All the acids had their greatest solvent action at concentrations between 10 and 30 per cent.

Frost³³ conducted tests on finished enamel surfaces, following the method of Landrum. He obtained results that checked those of Landrum. The results obtained by Landrum and Frost are shown in Fig. 14.

³⁰ R. D. Landrum, *Trans. Am. Ceram. Soc.*, **13**, pp. 494-501.

³¹ H. F. Staley, *Trans. Am. Ceram. Soc.*, **13**, p. 499.

³² E. P. Poste, *Trans. Am. Ceram. Soc.*, **17**, pp. 137-149; and **18**, pp. 762-766.

³³ Leon J. Frost, *Jour. Am. Ceram. Soc.*, **1**, p. 422.

In a third investigation Poste³⁴ studied the action of acetic, citric, and tartaric acids on grains of enamel. He found that the latter two acids were superior to acetic for testing the acid resist-

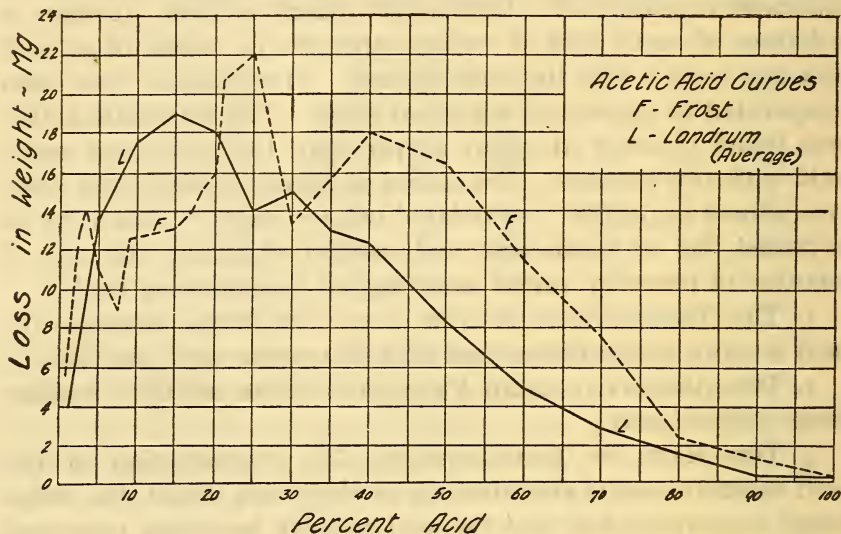


FIG. 14.—Loss in weight of enamels with acetic acid solutions of various strengths

ance of enamels, since the resistance does not vary much with concentrations in the region close to 20 per cent of acid.

WASHINGTON, November 11, 1919.

³⁴ E. P. Poste, Jour. Am. Ceram. Soc., 2, pp. 32-43.

